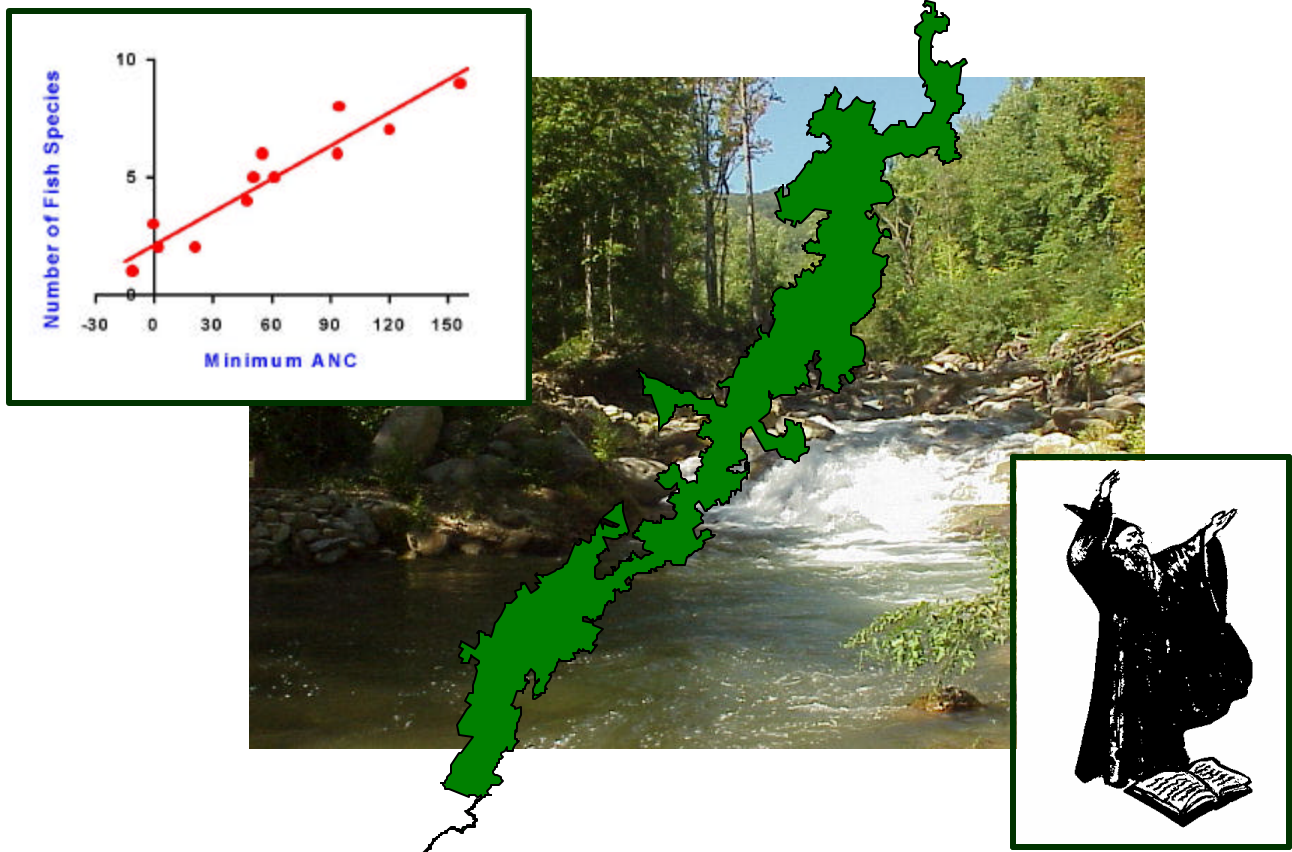


# **SNP:FISH**

## **Shenandoah National Park: Fish In Sensitive Habitats**

### **Project Final Report - Volume I**

### **Project Description and Summary of Results**



**A.J. Bulger**

**B.J. Cosby**

**C.A. Dolloff**

**K.N. Eshleman**

**J.R. Webb**

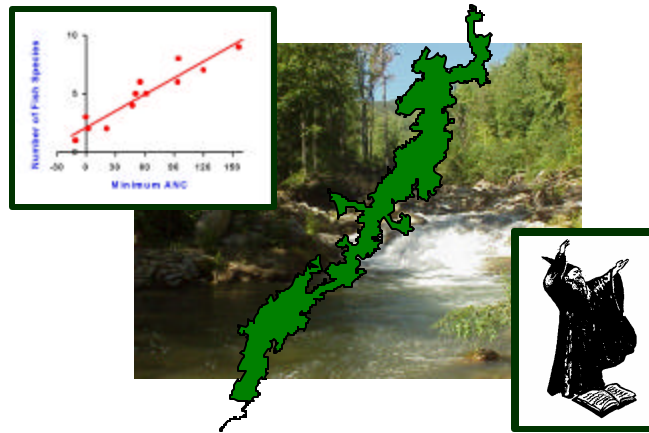
**J.N. Galloway**



# **SNP:FISH**

## **Shenandoah National Park: Fish In Sensitive Habitats**

### **Project Final Report - Volume I**



**A.J. Bulger<sup>1</sup>    B.J. Cosby<sup>1</sup>    C.A. Dolloff<sup>2</sup>**  
**K.N. Eshleman<sup>3</sup>    J.R. Webb<sup>1</sup>    J.N. Galloway<sup>1</sup>**

<sup>1</sup> Department of Environmental Sciences  
Clark Hall, University of Virginia  
Charlottesville, VA 22903

<sup>2</sup> Dept. of Fisheries and Wildlife Sciences,  
Virginia Polytechnic and State University  
Blacksburg, Virginia 24061

<sup>3</sup> University of Maryland, Center for Environmental Sciences  
Appalachian Laboratory  
Frostburg, MD 21532



**SNP:FISH**  
**Shenandoah National Park: Fish In Sensitive Habitats**  
**Project Final Report**

**A.J. Bulger      B.J. Cosby      C.A. Dolloff**  
**K.N. Eshleman      J.R. Webb      J.N. Galloway**

## **Acknowledgments**

This study was supported by the US National Park Service (NPS) under cooperative agreement CA-4000-2-1007, Supplemental Agreement #2, to the University of Virginia; and by the University of Virginia and Virginia Polytechnic Institute and State University.

During this project we received substantial assistance from staff at the Shenandoah National Park, including Dave Haskell, Julie Thomas, Tom Blount, Jim Atkinson, Bob Krumenaker, and, more recently, from Christi Gordon; they provided not only local expertise, but sound judgment. John Karish, NPS Chief Regional Scientist, provided sound judgment in addition to insight, determination, enthusiasm, and conscientious editing. Pat Thompson, Susanne Maben, Frank Deviney, and Cheryl Rhinehart, provided rigorous attention to detail, conscientious field efforts, hard work and good humor always. Our grad students could not have been better, and Kurt Newman, Ken Hyer, Todd Dennis, and Steve MacAvoy all exceeded our expectations for hard work and creativity for the Master's Degree work they did for this project. Our undergrad students also made substantial contributions, for which we very grateful. They are Michele Steg, Kerynn Fisher, Logan Martin, Karen Heys, Tim McLaughlin, Gary McLaughlin, Sophie Johnston, Sean Watts, Ricky Zaepfel, Bryna Cosgriff, Amy Luttrell, Gar Ragland, Jack McFarland and Dorothy Overpeck. Thanks to Charlie Stevens, Blain Hilton and Bob Shaffer for providing the fish eggs. Assistance in the field was provided by Marty Underwood, Chris Lotts, David Argent, Kelly Harpster, and Bob Hilderbrand. We thank Paul Angermeier and Dick Neves for their invaluable advise, insights, and comments throughout various stages of this work.



**SNP:FISH**  
**Shenandoah National Park: Fish In Sensitive Habitats**  
**Project Final Report, Volume I**

**Contents of Volume I**

**Page 1**            **Contents of Volumes II, III, and IV and the available CD-ROM**

**Page 3**            **Abstract**

**Page 5**            **Executive Summary**

**Prepared by** Arthur J. Bulger  
Dept. of Environmental Sciences  
Clark Hall, University of Virginia  
Charlottesville, VA 22903

C. Andrew Dolloff  
Dept. of Fisheries and Wildlife Sciences,  
Virginia Tech, Blacksburg, Virginia 24061-0321.

**Page 17**          **Chapter 1 - Project Overview and Summary of Results**

**Prepared by** Arthur J. Bulger and Bernard J. Cosby  
Dept. of Environmental Sciences  
Clark Hall, University of Virginia  
Charlottesville, VA 22903

**Page 51**          **Chapter 2 - Application of Research Findings for Resource Management in  
Shenandoah national Park Using the MAGIC model**

**Prepared by** Bernard J. Cosby  
Dept. of Environmental Sciences  
Clark Hall, University of Virginia  
Charlottesville, VA 22903

**Page 73**          **Appendix I - Maps of the SNP:FISH Catchments  
Catchment Boundaries, Stream Networks, Sampling Sites  
Distributions of Vegetation and Bedrock Geology**

**Prepared by** Rick Webb  
Dept. of Environmental Sciences  
Clark Hall, University of Virginia  
Charlottesville, VA 22903





**SNP:FISH**  
**Shenandoah National Park: Fish In Sensitive Habitats**  
**Project Final Report**

**A.J. Bulger      B.J. Cosby      C.A. Dolloff**  
**K.N. Eshleman      J.R. Webb      J.N. Galloway**

**Contents of Volumes II, III, and IV**

**Contents of Volume II**

**Chapter 3 - Synoptic Stream Water Chemistry**

**Prepared by Rick Webb**

**Chapter 4 - Discharge and Water Chemistry at the Three Intensive Sites**

**Prepared by Keith N. Eshleman and Kenneth Hyer**

**Appendix I - Watershed and Stream-Sampling Site Information**

**Prepared by Rick Webb**

**Appendix II - Analysis Methods and Data**

**Prepared by Rick Webb**

**Contents of Volume III**

**Chapter 5A - Influence of Water Quality and Physical Habitat on Brook Char and Blacknose Dace in Three Streams with Different Acid Neutralizing Capacities in Shenandoah National Park, Virginia**

**Prepared by C. Andrew Dolloff and Kurt R. Newman**

**Chapter 5B - Condition, Production, and Population Dynamics of Brook Char and Blacknose Dace in Acid-Sensitive Shenandoah National Park Watersheds**

**Prepared by C. Andrew Dolloff and Kurt R. Newman**

**Chapter 5C - Response of Brook Char (*Salvelinus fontinalis*), and Blacknose Dace (*Rhinichthys atratulus*) to Acidification in a Laboratory Stream**

**Prepared by C. Andrew Dolloff and Kurt R. Newman**

## **Contents of Volume III (continued)**

### **Chapter 5D - Extensive Inventory of Physical Habitat and Fish Populations in Five Streams with Different Acid Neutralizing Capacities in Shenandoah National Park, Virginia**

**Prepared by** C. Andrew Dolloff and Martin K. Underwood

## **Contents of Volume IV**

### **Chapter 6A - Susceptibility of the Early Life Stages of Brook Trout, *Salvelinus fontinalis*, and Adult Blacknose Dace, *Rhinichthys atratulus*, to Acidification in Shenandoah National Park**

**Prepared by** S.E. MacAvoy and A.J. Bulger

### **Chapter 6B - Susceptibility of Blacknose Dace, *Rhinichthys atratulus*, to Acidification in Shenandoah National Park**

**Prepared by** T. Dennis and A.J. Bulger

### **Chapter 6C - Stream Chemistry and Fish Species Richness in Shenandoah National Park**

**Prepared by** A.J. Bulger, M. Steg, T. Dennis and S.E. MacAvoy

### **Chapter 7 - Modelling the Biological Effects of Water Quality Changes in the Streams of the FISH Catchments**

**Prepared by** B.J. Cosby

**Electronic copies of all four volumes of this report** are included on the **available CD-ROM** that accompanies this report. The files are all Microsoft WORD document files (xxx.DOC), or Corel DRAW presentation files (xxx.SHW). Due to the large size of some of the files containing figures and graphical displays, the electronic copy of each volume consists of several files. All files for a given volume are collected in directories on the CD-ROM identified by the report volume number.

**Calibrated parameter files** for the intensively-studied FISH catchments and **an executable copy of the MAGIC:FISH model** are also included on the **available CD-ROM** that accompanies this report. The model was calibrated as described in Chapters 2 and 7 for the three intensively-studied FISH catchments. The executable model code and the average parameter file for each site (xxx.PAR) are stored in the MAGIC-FISH directory on the CD-ROM. The input files for the calibration, the successful fuzzy calibration parameter sets, and the summary statistics and model goodness-of-fit for the calibrations (xxx.OUT) are saved on the CD-ROM in separate sub-directories for each site (Paine Run, Piney River and Staunton River).

**SNP:FISH**  
**Shenandoah National Park: Fish In Sensitive Habitats**  
**Project Final Report, Volume I**

**A.J. Bulger      B.J. Cosby      C.A. Dolloff**  
**K.N. Eshleman      J.R. Webb      J.N. Galloway**

## **Abstract**

Surface waters in the Southern Appalachian mountains support a high diversity of fish species. Yet the Southern Appalachian Assessment concluded that 70% of sampled locations show moderate to severe fish community and/or habitat degradation, one cause of which is acidic deposition. The mid-Atlantic Highlands has one of the highest rates of acidic deposition in the US, and our research in forested headwater catchments in western Virginia has demonstrated that both chronic and episodic acidification occur in streams in the region. Our studies have also shown that changes in water quality accompanying acidification are related to observable biogeochemical characteristics of the landscape. The susceptibility of streams to acidification is largely geologically determined and empirical relationships can be used to classify sensitive landscape types. Rates of acidification are moderated by forest and soil biogeochemical processes and can be projected using the process-based MAGIC model. The effects of stream acidification on fish are documented in this report for the first time for streams in the Shenandoah National Park (SNP), VA. These effects can be observed at different ecosystem levels and can be quantified using regression models:

- 1) community-level effects (reduced species richness in streams);
- 2) population-level effects (increased mortality of brook trout, *Salvelinus fontinalis*); and
- 3) effects on single organisms (reduced condition factor of individuals).

Based on these results, we can now link water-quality changes to adverse effects (both lethal and sub-lethal) on fish in SNP streams. These linkages provide a unique resource with which we can construct conceptual and mathematical models that have both scientific and management utility; models that can aid our understanding of the complex interactions in the stream ecosystems and can quantify expected responses. The results of this study (and the computer model linking the chain of effects) provide the capability for park managers to incorporate acidification effects on fish as one component in any integrated analyses of the past, current, and future responses to acidic deposition of aquatic resources in the park.



**SNP:FISH**  
**Shenandoah National Park: Fish In Sensitive Habitats**  
**Project Final Report, Volume I**

**Executive Summary**

Prepared by  
**Arthur J. Bulger<sup>1</sup> and C. Andrew Dolloff<sup>2</sup>**

<sup>1</sup>**Department of Environmental Sciences**  
**University of Virginia**  
**Charlottesville, Virginia 22903**

<sup>2</sup>**Department of Fisheries and Wildlife**  
**Virginia Polytechnic and State University**  
**Blacksburg, Virginia 24061**

**Objectives**

The objectives of SNP:FISH (Shenandoah National Park: Fish in Sensitive Habitats) were:

- 1) to describe the water chemistry, physical habitat, and fish communities in selected streams in the Shenandoah National Park (SNP) in Virginia;
- 2) to determine if and how fish communities in these streams are influenced by stream acidification; and
- 3) to use current physical, chemical, and biological data to predict future trends in acidification and effects on stream biota.

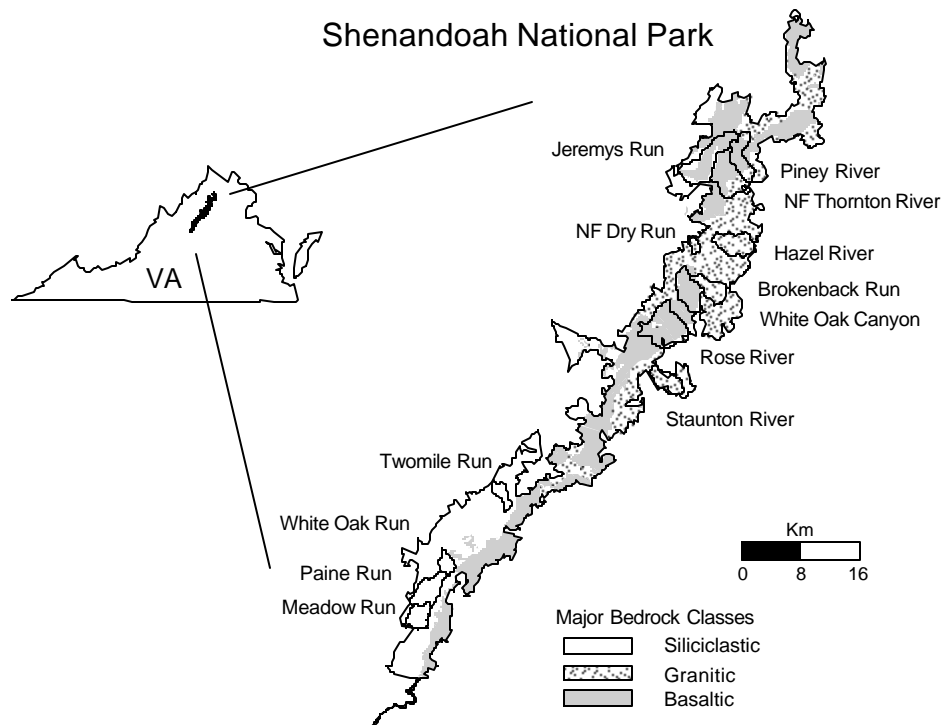
**Narrative Summary of Findings**

The SNP:FISH project was designed to account for both temporal and spatial variation in water chemistry and flow, habitat structure, and fish community response. Three streams of varying sensitivity to acidification (as measured by acid neutralizing capacity - ANC) were selected for intensive study over a three-year period. The streams and their respective ANC classes are: Paine Run, low ANC; Staunton River, medium ANC; and Piney River, high ANC. These streams

drain catchments underlain by three common bedrock types in SNP (each underlying about one-third of SNP catchments): siliciclastic, granitic, and basaltic bedrock, respectively, for Paine Run, Staunton River, and Piney River (Figure E-1, Table E-1). Five additional streams - three having low and two having medium ANC - also were sampled but at lower frequency than the three primary basins.

**Table E-1.** Mean values for selected water chemistry parameters from the three SNP:FISH intensive streams for the three years of the project. Means are presented (with standard deviations in parentheses) that are based on approximately 150 weekly samples for each stream. Episodic chemistry samples are not included.

	pH	ANC meq/L	Calcium meq/L
<b>Paine Run</b>	5.8 (.25)	5.9 (5.01)	31.3 (4.1)
<b>Staunton River</b>	6.7 (.24)	81.8 (18.5)	66.4 (6.0)
<b>Piney River</b>	7.1 (.16)	217.0 (67.8)	142.2 (19.0)



**Figure E-1.** Map showing streams (catchments outlined) covered in the report, and distribution of major bedrock classes in the Shenandoah national Park. Piney River (north district, high ANC), Staunton River (central district, intermediate ANC), and Paine Run (south district, low ANC) were intensively studied.

Water flow (stream discharge) was monitored continuously, and water chemistry was monitored weekly, episodically (associated with storm events), and synoptically (twice annually at multiple sites upstream from the main sampling stations) for the three year duration of the study. Fish habitats and fish communities were inventoried using the basinwide visual estimation technique; fish populations were inventoried each spring and fall in each of the three intensively studied basins. In situ fish bioassays (trout eggs and fry; adult blacknose dace) were performed in all three basins. Fish populations, habitat, and water chemistry also were sampled but at a lower frequency in the five additional basins. These two study designs allowed comparisons both within (3-basin intensive) and among (5-basin extensive) catchments.

Compared to the Adirondack Mountains or southern Norway, where hundreds of fish populations were lost by the 1980s, SNP streams are in the early stages of stream acidification, due in part to regionally thicker soils and their sulfate retention capacity. If present levels of acid deposition persist, it is likely that the negative biological effects of acidification demonstrated by this project will worsen.

Acidification effects result from interactions of atmospheric, geological, hydrological, chemical, and biological processes. Atmospheric processes deliver acidifying pollutants (sulfur, nitrogen oxides and ammonia) throughout SNP. In catchments underlain by relatively soft bedrock such as basalt, weathering rates produce sufficient acid neutralizing capacity (ANC) in streams such that stream acidity values remain above pH 7 (acid-neutral), and no negative biological effects result under baseflow or stormflow conditions. But in catchments where siliciclastic bedrock predominates and weathering rates are low, stream ANC values are typically low or even negative, and pH values as low as 5.0 are common. Fish in these unbuffered streams suffer the effects of both chronic and episodic acidification. In extreme situations, most if not all of a year-class may be lost if an acid-episode occurs when the fish are particularly vulnerable, such as during the egg and fry life stages.

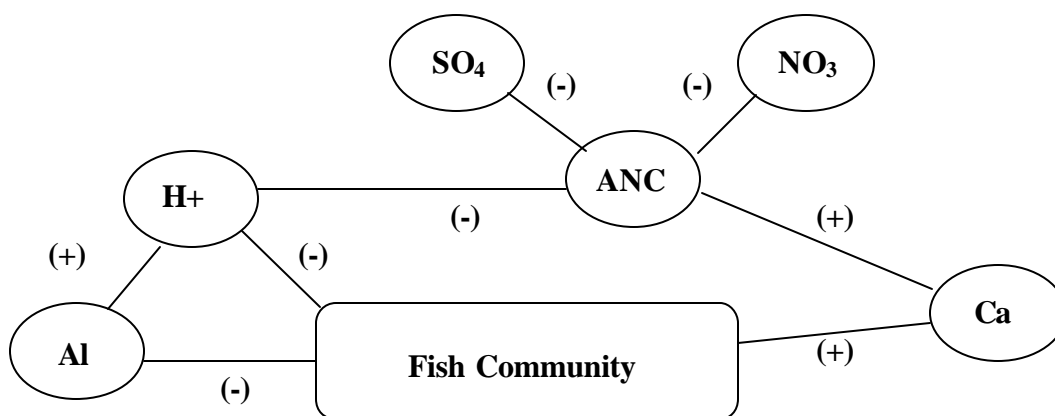
The amount of buffering is therefore critical to the long-term viability of fish populations. Buffering is a function of the type of bedrock and the acidity of rainfall. During storm events, water in streams consists of a mixture of pre-event or "old" water (ranging from poorly to well buffered) and unbuffered rain or "new" water. Simultaneous measurements of stream discharge and episode chemistry made in this project confirm that variations in flow regime were responsible for short term variations in stream water chemistry. In SNP, even episode discharge is often dominated by

pre-event water, which has been buffered by weathered minerals. So episodes, while still lethal to fish, may be less intense chemically (minimum pH reached) compared to glaciated areas further north, such as the Adirondack Mountains, with thinner soils.

The thicker soils of SNP also retain larger amounts of atmospheric sulfate, producing a temporal delay in regional acidification of streams. However, the soils' ability to retain sulfate is finite, and once saturated, all sulfate inputs will contribute to episodic acidification, perhaps intensifying SNP acid episodes. Base flow ANC values are also expected to decline. Local soils are approximately 70% saturated with sulfate now.

Except in extreme situations, differences in fish communities in acid-sensitive versus acid-insensitive watersheds cannot automatically be attributed to water chemistry alone. Information on habitat is necessary to characterize the potential to support fish communities. As confirmed by detailed analysis of basinwide habitat data, habitat quality was similar across all three intensively studied streams. With a few important exceptions, the ANC of stream water decreased with increasing distance upstream. Thus, the weekly and episodic chemistry data collected at the Park boundary provide conservative estimates of acidification of the waters within SNP.

Low-pH water interacts with the living and non-living elements of the catchment in two critically important ways (Figure E-2). First, low pH can directly influence fish mortality by disrupting ion regulation. Second, low pH mobilizes aluminum which, although essentially non-toxic at high pH,



**Figure E-2.** Conceptual model of direct and indirect acidification effects on fish communities. As any variable increases in magnitude, it produces the indicated effect (positive or negative) on the receptor. Acidic pollutants (SO<sub>4</sub> and NO<sub>3</sub>) lower ANC, resulting in an increase in hydrogen ion (H<sup>+</sup>) concentration (= increase acidity = lower pH) with direct toxic effects on fish. Increased H<sup>+</sup> mobilizes aluminum (directly toxic to fish) from soils. Calcium directly counters aluminum and acid toxicity, and it elevates ANC.



is highly toxic to fish under acidic conditions. Fish in streams that drain poorly buffered soils that are high in aluminum are therefore particularly vulnerable to any increase in acidification.

Stream water calcium, which is mostly derived from mineral weathering, also interacts with the biotic and abiotic elements of the catchment in important ways. Calcium directly counters the effects of both low pH and aluminum and contributes to ANC. The physiological effects of calcium are so potent over the range of 0-150 µeq/L (within the observed range of calcium in the intensive streams) that small increases in the concentration of dissolved calcium produce dramatic increases in fish survival. At concentrations above 150 µeq/L, the effects on fish survival are less pronounced following additional increases in calcium.

### **Specific Findings**

#### *Mortality of brook trout eggs and fry.*

During the six 1-3 month-long brook trout bioassays in each intensive stream, mortality was observed from three sources in one or more streams: drought and fungal infection (one bioassay), flood and sedimentation (three bioassays), and acidification (three bioassays). Predation on eggs, a potential source of mortality, was prevented by the bioassay design. The bioassays used large sample sizes, 1000-2000 individuals per stream per bioassay, placed into artificial gravel nests, mimicking natural gravel trout nests, which could be withdrawn at intervals without disturbing all the nests, minimizing handling stress.

#### *Drought.*

Low stream flow was the ultimate source of mortality in the fall, 1993, bioassay. Mortality in was uniformly high in all streams within seven days after placement, due to fungal infection (probably *Saprolegnia*), secondary to very dry conditions. This is a common source of trout egg and fry mortality when low flow prevents adequate flushing of gravel nests.

#### *Flood.*

High flow was the source of mortality in the spring, 1995, bioassay. It was begun on 1/13/95; a massive hydrologic event occurred in all three streams two days later. It was clear from inspection after the event that the artificial gravel nests, the cages that contained them, and even the protective devices, had been agitated substantially during the flood, especially at Paine and Piney.

The artificial nests had also trapped much sediment, interfering with the flow of fresh water after the flood. Steep declines in survivorship, similar at all three sites, are probably best attributed to mechanical damage plus suffocation (due to sediment in the nests) resulting from flood conditions. Flood is also regarded as a common natural source of mortality for young trout still in nests.

#### *Acid stress.*

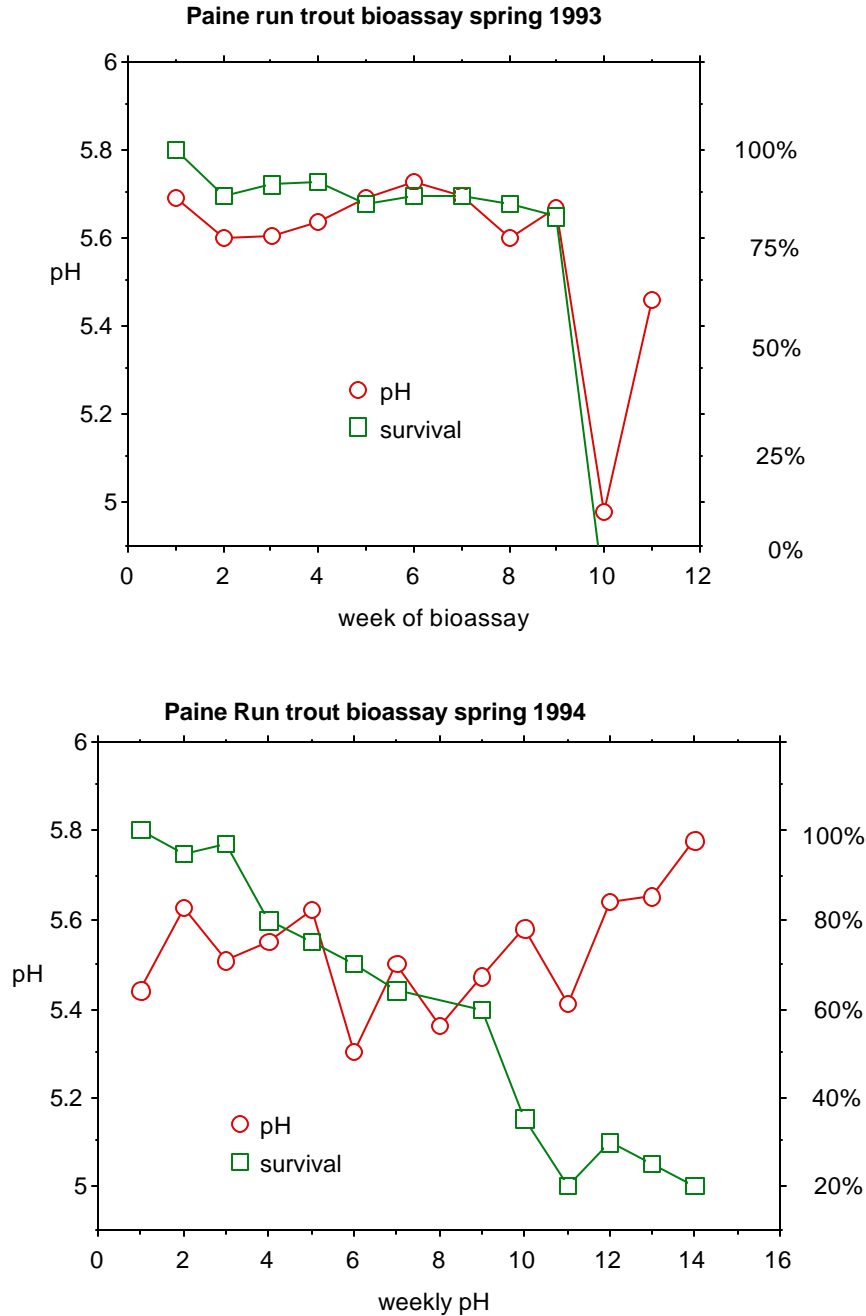
Differential mortality of trout occurred among the study streams during four of the six bioassays (fall 1992, spring 1993, spring 1994, and fall 1994). In each of these four, trout in Piney River (high-ANC) showed higher survival rates than trout in Paine Run (low-ANC). The most likely source of differential mortality in two bioassays is episodic acidification, and chronic acidification plus sedimentation in the other two bioassays. Compare the pH ranges during the two example bioassays in Figure E-3: pH remained between 5.8 and 5.6 for most of the first bioassay, followed by a sharp drop. In the second bioassay, there were no sharp drops, but pH was nearly always below 5.6. The mortality in these bioassays can be considered as acute or episodic in the first case, and chronic in the second.

#### *Acute Acid Stress.*

The spring, 1993, bioassay at Pine Run typifies acute acidification mortality (Figure E-3). The spring was fairly dry until large hydrological events occurred in all three streams, killing all remaining fry at the low-ANC stream, Paine Run, where survivorship declined sharply from 80% to 0%, coincident with the sharp drop in pH (and peak in toxic aluminum concentration, Chapter 6A). This indicates that pre-event baseflow, maintained by groundwater, was not toxic, while acidic storm flow was toxic. Trout survivorship remained high at Piney River during this bioassay, despite increased storm flow, no doubt due to the greater ANC at Piney River, which prevented the pH from dropping lower than 6.6; toxic aluminum concentrations there were below detection limits.

#### *Chronic Acid Stress.*

The spring, 1994, bioassay at Paine Run illustrates chronic acidification mortality (Figure E-3). Survivorship in Paine Run showed a steady decline and was significantly lower than that at Piney River. Four moderate hydrological events at Paine Run kept the pH between 5.6 and 5.3 for most of bioassay, with no sharp pH drops. pH increased after most of the fish had died. Mortality here may best be attributed to accumulated stress associated with acidification of streamwater.



**Figure E-3.** Two bioassays illustrating mortality due to acute acid stress (top) and chronic acid stress (bottom). Note that in the upper example, pH stays above 5.6 until a sharp drop occurs, associated with sudden mortality, while in the lower example pH stays between 5.6 and 5.3, with no sharp drop, associated with gradual mortality. Survival is estimated by periodic removal without replacement of pairs of artificial nests from a large sample of nests, to avoid disturbing all the nests, which can cause stress. Apparent increases in survival over time are due to differences in survival among nests removed in adjacent weeks.

#### *Chronic effects on brook trout.*

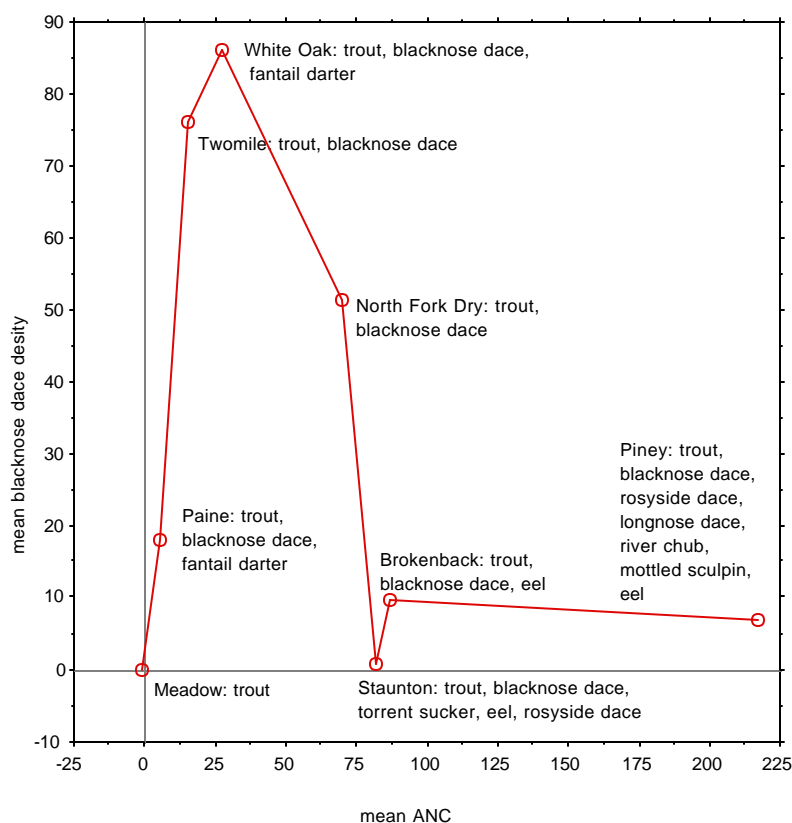
Several other measures of the overall health of fish populations are derived from the fish community surveys described in Chapter 5. These integrate effects over longer time periods than the episodic responses of trout early life stages described above. Among the three intensive streams, the contrasts between brook trout in Paine Run (low ANC) versus Piney River (high-ANC) are the clearest. Paine Run trout show a combination of poor condition of individual fish, lower mean weight, lower population density and lower rate of annual production versus trout in Piney River. This suggests that poor water quality may limit trout growth in Paine Run. Since density of trout was always lower in Paine versus Piney, it does not appear that competition limits trout growth in Paine Run, and no combination of habitat characteristics appears to explain the differences.

#### *Chronic effects on blacknose dace.*

Among the three intensive streams, blacknose dace in Paine Run (low ANC) had significantly lower condition factor and mean weight, versus Piney River (high ANC) and Staunton River (mid-ANC) blacknose dace, which were similar to each other. Further, there was a very strong relationship across multiple streams in dace condition factor, which was incorporated into the predictive models in Chapter 7.

#### *Chemical and biotic effects on blacknose dace density across an ANC gradient.*

Figure E-4 shows the density of dace populations in the eight streams (three intensive and five extensive streams) plotted versus baseflow ANC, and indicates the other species present in each stream. Blacknose dace are more sensitive to acidification than brook trout; however, it is likely that blacknose dace are more tolerant to acidification than many other fish species which are absent from low-pH streams where blacknose dace are still present. Blacknose dace densities peak in the lower half of the ANC range, in the absence of both potential competitors (other members of the cyprinid family: rosyside dace, longnose dace, river chub) and in the absence of predatory American eel. It may be that dace are limited by acid water chemistry on the one hand, and biotic (competition and/or predation) factors on the other. The blacknose dace population in Meadow Run, the lowest ANC- stream of those studied, declined since the study began and is now regarded as extirpated from that stream.



**Figure E-4.** Blacknose dace density (number of individuals per 100 m<sup>2</sup> of habitat) in the FISH project's three intensive and five extensive streams, versus mean ANC. Other fish species present in each stream are shown after the stream name on the graph.

#### *Acid sensitivity of blacknose dace versus brook trout.*

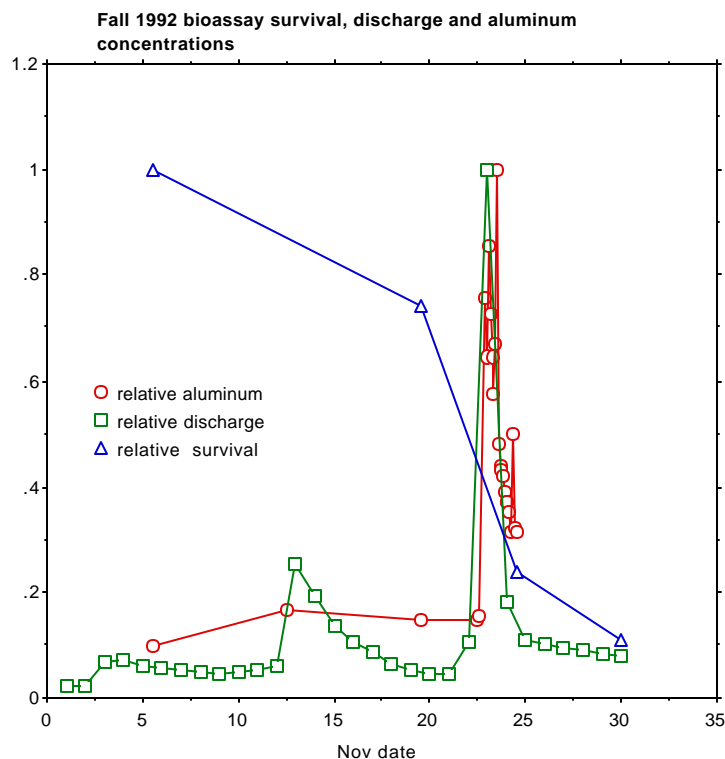
The differences between these two species is less clear-cut than often depicted. Brook trout adults are more tolerant of acidification effects than blacknose dace adults; in both species the young are regarded as more sensitive than adults. Yet this study has shown that brook trout young are more sensitive than blacknose dace adults: during the fall 1994 bioassay in Paine Run, significant mortality occurred among brook trout fry, while, simultaneously, blacknose dace maintained in cages nearby showed 100% survival.

Blacknose dace spawn in the summer, when ANC often peaks in SNP, so eggs and very young fry are not present in spring and fall when acid episodes are worst. Thus, in the early stages of regional acidification, when through reproductive timing, blacknose dace young are isolated from the worst acid events and survive, there may already be negative effects on brook trout young;

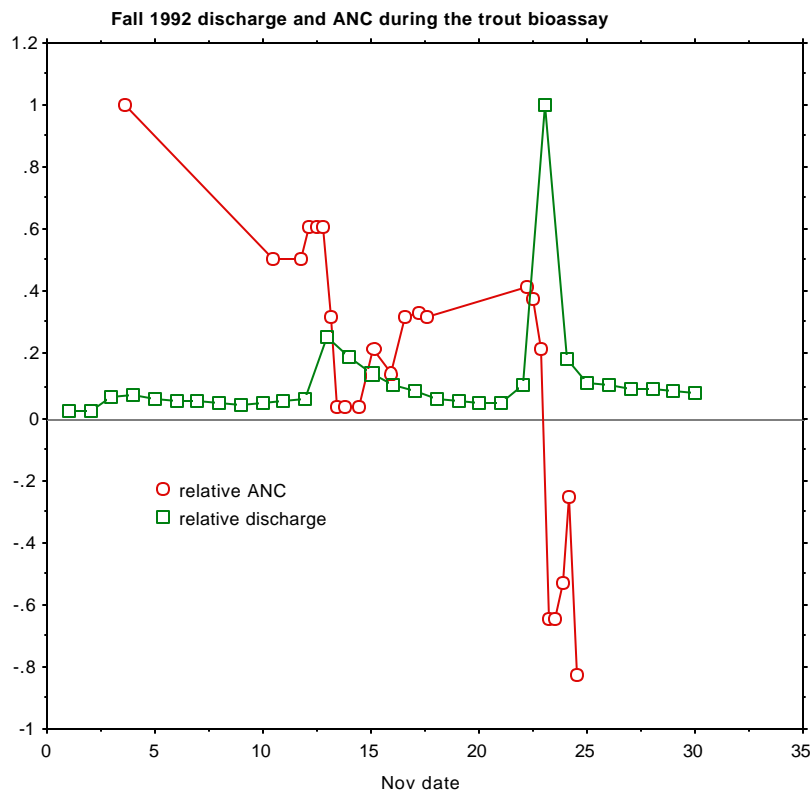
thus, the presence of the more sensitive species (blacknose dace) does not necessarily mean that the more tolerant species (brook trout) is still unaffected. Furthermore, the blacknose dace is often represented as an acid-sensitive species; the relationships in Figure E-4 suggest that in fact blacknose dace is one of the more acid-tolerant species SNP, since they are present in low-ANC streams where other fish species are absent.

#### *Rapid hydrochemical and biological responses in episodes.*

The last figures in this section (Figures E-5 and E-6) illustrate the rapid responses to hydrologic episodes. In the absence of high-frequency sampling, it would be difficult to interpret the sudden mortality of brook trout during the bioassay. In Figure E-5, note the rapid response of toxic aluminum to discharge, and that the episode signals (discharge and aluminum peaks) last only about two days. In Figure E-6, note that the ANC troughs lag only very slightly behind the discharge peaks.



**Figure E-5.** Fall, 1992 bioassay trout survival, discharge and aluminum concentrations. Since the variables have very different ranges, values for each are shown as relative to the maximum value for each variable. Note the rapid response of both toxic aluminum concentrations and mortality to discharge.



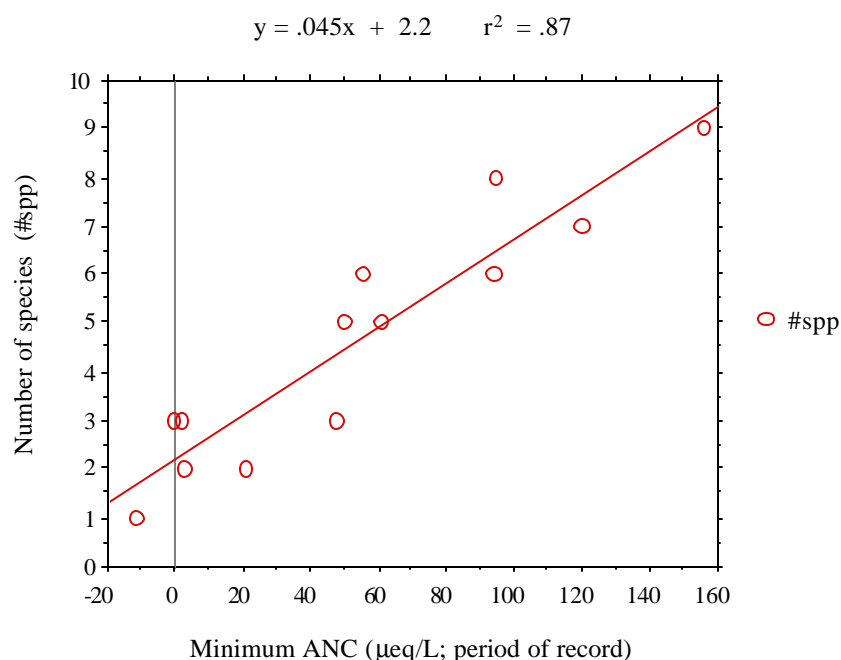
**Figure E-6.** Fall, 1992 discharge and ANC during the trout bioassay in Paine Run. Since the variables have very different ranges, values for each are shown as relative to the maximum value for each variable. Note that ANC troughs lag slightly behind discharge peaks.

#### *Differences in fish species richness.*

Fish species differ in their tolerance to acid conditions. Acidification has been shown to reduce fish species richness (defined simply as the number of species in a defined area) by eliminating sensitive species from fish communities.

Since SNP contains streams with low ANC, and receives substantial acid deposition, the fish species richness of at least some of its streams may have been lowered by acidification. However, the fish community records of SNP streams are too recent (begun in the 1980s) to demonstrate loss of species from streams. There is, nevertheless, a very strong relationship between the number of fish species present in streams now and their acid-base status, such that

streams with low ANC host fewer species (Figure E-7). This relationship suggests, that if stream ANC is lowered in SNP, species will disappear from SNP streams. The first recorded is the blacknose dace population in Meadow Run (Figure E-4).



**Figure E-7.** Relationship between number of fish species (#spp) and Minimum ANC recorded in SNP streams; data derived from SNP Fisheries Management Plan (FMP) and the FISH project.

This last result, the strong dependence of fish species richness on the acid-base status of stream water, may be the most important finding of the SNP:FISH project. Fish diversity in the Southern Appalachians is high. Of the approximately 950 species of freshwater fish in North America, about 485 species are found in the Southeast. The total numbers of freshwater fish species per state in the region range from 107 in Maryland, to 307 in Tennessee. That species richness in SNP approaches zero as minimum stream ANC become slightly negative is cause for grave concern within the park. If this result holds for the rest of the southern Appalachian region as well, the potential (or currently realized) loss of biodiversity in fish communities due to acidification may be significant.



**SNP:FISH**  
**Shenandoah National Park: Fish In Sensitive Habitats**  
**Project Final Report, Volume I**

**Chapter 1**

**Project Overview and Summary of Results**

**Prepared by**

**A.J. Bulger and B.J. Cosby**

**Department of Environmental Sciences**

**University of Virginia**

**Introduction**

Permanent water bodies are conspicuous features in the southern Appalachian mountains. The mean density of streams and river channels is more than 9m of length per hectare of land, and river and lake surface is at least 1.5% of the total surface area of the southern Appalachians. Water bodies are regarded by residents as extremely important, and multiple uses include drinking water, transportation, agriculture, flood control, hydroelectric power, wildlife observation, waterfront human habitation, fishing, other aquatic recreation (SAMAB 1996). Fish diversity in the Southern Appalachians is high. Of the approximately 950 species of freshwater fish in North America, about 485 species are found in the Southeast (Jenkins and Burkhead 1993; Walsh et al. 1995). The total numbers of freshwater fish species per state in the region range from 107 in Maryland, to 307 in Tennessee (Jenkins and Burkhead 1993).

While there is general agreement that water quality has improved in the southern Appalachians since the adoption of the Clean Water Act in 1972 (which required treatment and controls for most municipal and industrial discharges), those sources of pollution not covered by the act (e.g., acid deposition, storm water runoff, sediment contamination, and toxic spills) continue to have adverse effects on surface waters in the region. A regional survey conducted as part of the Southern Appalachian Assessment concluded that 70% of sampled locations on streams show moderate to severe fish community and/or habitat degradation, and that about 50% of the stream length in WVA and VA show structural habitat impairment (SAMAB 1996).

The Mid-Atlantic Highlands has one of the highest rates of acid deposition in the US (Herlihy et al. 1993, 1996). The region most at risk from acid deposition is located along the Appalachian Mountain chain from the Adirondacks in New York to the Southern Blue Ridge in Georgia (NAPAP 1990). There have been significant historical declines in the acid neutralizing capacity of stream waters (acidification) in the region as a result of chronic acid deposition (Kaufmann 1988, National Stream Survey). This acidification is a conspicuous threat to the fish populations in the lakes and streams of the region. While all species are affected to a greater or lesser degree, those species important for angling (and its associated recreational values) are most often the species of primary concern in assessing acidification effects. In upland streams and lakes, these are primarily three trout species: brook trout, brown trout, and rainbow trout (reproducing populations of any of the three are often referred to as "wild" trout). Of the three, native brook trout is the most acid tolerant, brown trout introduced from Europe is intermediate in acid tolerance, and rainbow trout introduced from the western US is most sensitive.

Approximately 40% (6 million hectares) of the area the southern Appalachian mountains is in the range of wild trout, with up to 53,000 km of potential wild trout streams (SAMAB 1996). Virginia alone accounts for 39% of regional trout stream length, with 32% in North Carolina, 10% in Georgia, 10% in Tennessee, 7% in West Virginia, 2% in South Carolina, and 0% in Alabama. The Southern Appalachian Assessment concluded that about 27% of all wild trout stream miles in the southern Appalachian mountains are in landscapes that are moderately vulnerable to acidification, and approximately 59% are in areas that are highly vulnerable to acidification (SAMAB 1996).

The finding that more than 85% of all wild trout streams in the southern Appalachians are in landscapes that are either moderately or highly vulnerable to acidification raises a number of urgent concerns best summarized by the questions: Are there currently adverse effects on fish in southern Appalachian streams as a result of acidification? How extensive are the effects and how long have they been occurring? What are the future trends in responses likely to be?

An analysis of current, reconstructed, and projected future fish responses in this acid sensitive landscape requires three components: 1) a scheme for relating the responses of fish to changes in stream water quality (fish responses considered should include individual, population and community responses and both lethal and sub-lethal effects); 2) observations of current water quality and fish responses in a regionally representative sample of streams (to establish

current conditions and to calibrate models of fish responses to water quality changes); and 3) a biogeochemical model for forecasting and reconstructing water quality, and therefore fish status, for the streams (including the additional data necessary for model calibration and implementation - atmospheric deposition, soil chemistry, etc.).

For the past twenty years, we have been studying the effects of acidic deposition in the mountains of Virginia. Our research has focused on processes at various spatial scales from plot to hillslope to catchment to landscape, and has covered the temporal scale from individual storm processes (hours) to long-term monitoring (decades). We have developed and sustained two closely coordinated research and monitoring programs at the University of Virginia that focus on the biogeochemistry of forested mountain watersheds in western Virginia: the Virginia Trout Stream Sensitivity Study (VTSSS) and the Shenandoah Watershed Study (SWAS).

The VTSSS program was initiated in the spring of 1987. An initial survey was conducted in which stream water quality was sampled for 344, or about 78%, of the state's identified native brook trout streams. The streams not included in the survey were those known to have substantial direct human disturbance in the watershed. Analysis of the survey data disclosed a strong correlation between local geology and the acid-base status the streams (Webb et al. 1994). The surveyed streams were subsequently stratified by geology and a representative subset selected for long-term water-quality monitoring. The VTSSS program presently includes 55 streams, mostly located on National Forest lands, that are sampled on a quarterly basis. Stream water samples collected for the VTSSS and SWAS programs are analyzed for sulfate, nitrate, chloride, hydrogen ion, calcium, magnesium, potassium, and sodium, ANC and pH. Dissolved organic carbon (and thus organic acidity) in these streams is negligible. Details of analytical and quality assurance methods and are posted on the SWAS-VTSSS website at <http://wsrv.clas.virginia.edu/~swasftp>.

The SWAS program was initiated in 1979 as part of a study of biogeochemical cycling within forested watersheds and their responses to anthropogenic perturbations. Stream water quality and discharge data and atmospheric deposition data are available on a weekly basis for two sites in the southern part of Shenandoah National Park (SNP) for the 21 year period from 1979 to the present (the longest continuous record of stream water quality data in a national park, and among the longest anywhere in the US). Additional weekly sampling sites have been added over the years in SNP resulting in 3 sites for which weekly streamwater and wet deposition data

are available for at least 11 years, and 6 sites for which weekly streamwater data are available covering a period of at least 6 years. There is an NADP/CASTNet site located in SNP. The SWAS program presently includes six streams that are sampled on a weekly basis and nine streams that are sampled on a quarterly basis. The SWAS quarterly sampling is scheduled to coincide with VTSSS quarterly sampling. In both programs, quarterly stream samples are taken during the last weeks of January, April, July and October.

In the course of our research (and deriving directly from it), we developed a simulation model of the acidification process. The Model of Acidification of Groundwater In Catchments (MAGIC, Cosby et al. 1985a-c) was the principal model used by the National Acid Precipitation Assessment Program (NAPAP) scientists in the 1991 assessment of potential future damage to lakes and streams in the eastern United States (NAPAP 1991, Thornton et al. 1990). The validity of the model has been confirmed by comparison with estimates of lake acidification inferred from paleolimnological reconstructions of historical lake changes in pH (Sullivan et al. 1991, 1996) and with the results of several catchment-scale experimental acidification and de-acidification experiments (e.g., Cosby et al. 1995, 1996). MAGIC has been used to reconstruct the history of acidification and to simulate the future trends on a regional basis and in a large number of individual catchments in both North America and Europe (e.g., Lepisto et al. 1988; Whitehead et al. 1988; Cosby et al. 1989, 1990, 1994, 1996; Hornberger et al. 1989; Jenkins et al. 1990a-c; Wright et al. 1990, 1994; Norton et al. 1992).

## **Project Goals**

In light of the sensitivity of the Appalachian landscape to acidification effects (with associated adverse impacts on fish populations) and our extensive hydrogeochemical research and monitoring activities relating to the effects of acid deposition in the mountains of Virginia (including the Shenandoah National Park), we set as the broad goal of this project the development of an integrated multidisciplinary assessment of chemical and biotic linkages in the context of the past, current and future acidification responses of streams in the Shenandoah National Park.

The focus of the assessment is fish community responses to stream acidification. There are considerable advantages in using fishes as biotic indicators of acidification. 1) Fishes are a valuable resource, and the historical composition of fish communities is relatively well known

for many streams. 2) The mechanisms of acidification effects on fish are direct and unambiguous: both elevated hydrogen ion (low pH) and aluminum (mobilized by acidification) are toxic to gill membrane processes responsible for blood electrolyte balance. The causal chain includes the deposition of sulfate and nitrate and their effects on pH and alkalinity, and the resulting mobilization of toxic aluminum; thus the effects can be traced from atmospheric transport to gill membrane dysfunction.

The advantages of this integrated approach are that the linkages between aquatic chemistry and fish responses have been established using an extensive database through which chemists, hydrologists, biologists, habitat structure analysts, modelers, and managers have access to the same information. Additional advantages of the integrated approach are coordination (standardization) of field and laboratory techniques, ready exchange of information and ideas, and cost-savings and efficiency through the use of shared data. The strategy has been to build on existing monitoring and research activities in the Environmental Sciences Department at the University of Virginia while adding new components designed to detect fish responses to acidification. The product of this effort is a research and assessment program that has documented and increased our understanding of acidification impacts on fish communities in headwater streams in western Virginia, and in the Shenandoah National Park in particular. Predictive models (both empirical and process-based) have been developed to estimate impacts on fish communities under changing acidification scenarios. These models are based on a comprehensive review of lab and field tolerances of fish species in the park, and provide managers with decision-making tools for assessing current and potential future effects of acidification on fish species in the park..

## **Project Objectives**

The specific objectives of SNP:FISH, therefore, were:

- 1) to describe the water chemistry, physical habitat, and fish communities in selected streams in the Shenandoah National Park (SNP) in Virginia;
- 2) to determine if and how fish communities in these streams are influenced by stream acidification; and
- 3) to use current physical, chemical, and biological data to predict future trends in acidification and effects on stream biota.

### **Acid deposition effects on fish.**

"Acid Rain" is a term in common use which implies the deposition of acid materials in wet precipitation (rain, snow, fog, cloud) as well as in the dry precipitation of dust and gases; scientists prefer to use "acid deposition" for this process, because it explicitly includes dry as well as wet deposition; indeed, deposition of acid materials in dry form is often equal to the amount deposited in wet form. Acid deposition is responsible for the loss of hundreds of fish populations in Europe and North America.

The effects of acid deposition on fish involve the interaction of complex processes operating at a range of different spatial scales, from atmospheric transport to cell membrane transport. Nevertheless, the interaction of these processes can be summarized in an outline consisting of five major points, as follows.

#### *1) The source of the acid: fossil fuels.*

The burning of fossil fuels releases sulfur and nitrogen oxides into the atmosphere, where they are converted to sulfuric and nitric acids. These acidic materials may be transported long distances in the atmosphere before they are deposited in wet or dry form on landscapes.

#### *2) Landscapes sensitivity: geologic setting.*

Whether or not acidic deposition produces negative effects on the animals living in streams and lakes depends largely on the bedrock geology of their catchments. In landscapes underlain by limestone (carbonate bedrock), which provides substantial buffering of acidity, negative effects due to acidification are neither expected nor seen in water bodies. Basaltic, granitic, and siliciclastic (such as sandstone) bedrock types represent a series of decreasing levels of buffering capacity, such that modest amounts of acidic deposition produce conspicuous negative effects in sandstone catchments. Since buffering capacity ultimately depends on the weathering of acid-neutralizing material from the bedrock, hard bedrock types produce less buffering capacity for streams than soft bedrock types. Mountains by their very nature are more resistant to weathering than surrounding lowlands (that's why the mountains are still there), so mountain streams and lakes are usually the most sensitive to acidification due to the lower

buffering capacity of their catchments. In contrast, large valley streams and lakes are often the recipients of upstream weathering products, and are often less sensitive to acidification as the result of their greater buffering capacity.

If the bedrock types underlying a given landscape unit are a heterogeneous mixture, in terms of their acid-neutralizing capacity, there will be different responses among the water bodies and fish communities in the landscape, even under identical acidic deposition regimes.

### *3) The role of aluminum: metabolic poison.*

Aluminum is the most abundant metal on the earth's surface, and the third most abundant element. It is non-toxic and insoluble under acid-neutral conditions, but very toxic to fish and other aquatic species under acidic conditions; unfortunately, the solubility of aluminum increases exponentially as pH falls below 5.6; its maximum toxicity occurs at about pH 5.0. The deposition of acids results in the release of aluminum from soils, which is carried in solution to streams and lakes. Both the aluminum and the hydrogen ion (derived from sulfuric and nitric acids) are toxic to fish, but in most streams and lakes the aluminum is the primary lethal agent; fish can survive more acidic conditions i.e., lower pH) in the laboratory in the absence of aluminum.

### *4) Site of toxic action: fish gill.*

The site of the toxic action of both hydrogen ion and aluminum is the fish gill. The gill is a complex organ responsible for oxygen and carbon dioxide exchange, as well as maintaining the proper salt and water balance the fish's body. It is this later function which is always compromised by acid and aluminum stress; respiration is also compromised at higher concentrations of aluminum.

Freshwater fish maintain salt (sodium chloride) in their blood at concentrations similar to those in humans and most other vertebrates. The proper functioning of most body cells, and especially blood cells in this context, depends on keeping salt concentrations in body fluids within rather narrow limits. Since salt concentrations in the blood are much higher than the fresh water in which they swim, fish constantly lose a small amount of sodium and chloride from the blood by passive diffusion across the thin skin of the gills. The lost sodium and chloride are replaced by an energy-requiring process (active transport) using biochemical "pumps" in the gill

membranes which transport sodium and chloride from low concentration in the external stream water to higher concentration in the blood.

Aluminum and hydrogen ion poison the biochemical pumps which transport sodium and chloride into the body; they also weaken the junctions between gill cells, making them leak more sodium and chloride than they otherwise would. The rapid loss without replacement of sodium and chloride produces a cascade of negative physiological effects in the body.

It is a common misconception that stream acidification causes acidification of fish blood, with negative effects on oxygen transport; this does not occur at observed levels of acidification in nature which produce fish death.

#### *5) Cause of death: circulatory collapse.*

The key indicators of incipient mortality under acute acid and aluminum stress are the concentrations of sodium and chloride in the blood plasma. When either or both (sodium and/or chloride) fall more than 30% below normal, death occurs within hours.

The proximal cause of death is electrolyte dilution of the blood plasma. This causes blood and body fluid disturbances which ultimately kill the fish through circulatory collapse. Under normal conditions, plasma electrolyte concentrations and body cell electrolyte concentrations are in equilibrium. Under acute acid stress, electrolytes are lost more rapidly from the blood plasma than from blood and muscle cells; as a result, there is an osmotically-driven shift of water to the cells from the plasma; blood plasma volume may drop as much as 30%; at the same time, the red blood cells swell due to the osmotically-driven shift of water from the plasma; the result is a doubling of blood viscosity. The heart is unable to circulate this much thicker blood at a rate sufficient to supply oxygen to body tissues, including the heart itself, so the fish dies of circulatory collapse secondary to electrolyte imbalance.

### **Selection of Study Sites in Shenandoah National Park**

Shenandoah National Park (SNP) is in the Blue Ridge physiographic province, on the eastern edge of the central Appalachian Mountains. SNP provides the opportunity for a comparative investigation of acidification effects on fish communities, due to the presence of a population of streams with a wide range of sensitivity to acid inputs. Acid sensitivity of streams is usually defined in terms of stream ANC (Acid Neutralizing Capacity), and several authorities



have defined classes of acid sensitivity based on criterion ANC values. Altshuller and Linthurst (1983), Winger et al. (1987), and Knapp et al. (1988) have used the criterion of ANC concentration of  $< 200$  meq/L for the identification of acid-sensitive surface waters; this would include most SNP streams. Lynch and Dise (1985) used a more stringent ANC concentration of  $< 100$  meq/L. ANC concentrations of  $< 50$  meq/L were used by Gibson et al. (1983) and Schindler et al. (1985) to identify extremely sensitive surface waters.

Atmospheric inputs of acidic pollutants to SNP are typical of the central Appalachian Mountains, which receive one of the highest rates of acidic deposition in the country (Baker et al., 1990; Herlihy et al., 1993). In 1990, the volume-weighted pH measured in precipitation at National Acidic Deposition Program (NADP) sites in the region was 4.1 - 4.3 (NADP, 1991). Sulfate loading at the NADP site in SNP has consistently been among the highest measured in United States national parks (NADP, 1986-1991). An unpublished comparison of precipitation measurements obtained for four locations in SNP suggests that sulfate deposition levels are similar throughout the park.

Acid-sensitive streams were first documented in SNP in the late 1970s (Hendrey et al., 1980). Synoptic stream-water surveys in 1982-83 (Lynch and Dise, 1985) revealed an ANC range in SNP streams from 0 to over 200 ueq /L, and showed that stream-water ANC in individual streams is closely associated with local bedrock type. Differences among catchments in bedrock weathering rates, mineral composition, and soils result from differences in bedrock composition, are responsible for surface waters with differing ANC concentrations. The three major bedrock classes in SNP are siliciclastic, granitic, and basaltic metamorphic assemblages of the Precambrian or early Cambrian eras (Gathwright, 1976); they yield streams with low ANC (0-20 ueq L<sup>-1</sup>), intermediate ANC (60-100 ueq L<sup>-1</sup>), and relatively high ANC (150-200 ueq L<sup>-1</sup>), respectively. Fish communities also respond to differences in bedrock geology, operating through stream chemistry. Data compiled by the SNP Fisheries Management Program (Atkinson, 1994) and the SNP:FISH project also indicate a strong positive correlation between the number of fish species in individual streams and stream ANC (Chapter 6C).

The Shenandoah Watershed Study (SWAS) selected two streams, White Oak Run and Deep Run, both in the low-ANC siliciclastic class, for weekly sampling beginning in late 1979. Ryan et al. (1989) observed decreasing trends in stream-water pH and ANC consistent with acidification for these streams from 1980 to 1987. Cosby et al. (1985) determined that more than

50% reduction in acid inputs is required to achieve a reversal or stabilization of ANC status among the population of watersheds represented by White Oak Run. Webb et al. (1989) reached similar conclusions using a different approach (a linear titration-model projection), and a data set of more than 300 native brook trout streams in SNP and the larger western Virginia mountain region.

### *Study Design.*

The SNP: FISH proposal called for three intensively studied streams to provide information on high-frequency temporal variation within the stream sensitivity categories. These streams are referred to as the "intensive streams", and are the sites for bioassays, discharge records, and automated water sampling at 8-hour intervals, plus episode-triggered, 2-hour intervals. The proposal also called for additional streams to provide a wider geographic coverage of SNP streams, but sampled at lower frequency. These are referred to as the "extensive streams". Candidate streams in ANC and geological classes are shown in Table 1-1.

**Table 1-1.** SNP\_FISH Project, Candidate Streams in Geologic and ANC Classes

<b>Siliciclastic</b> Sedimentary <i>Chilhowie</i> ANC = 0 - 25 ueq/L	<b>Granitic</b> Igneous <i>Pedlar, Old Ragg</i> ANC = 40 - 100 ueq/L	<b>Basaltic</b> Extrusive Igneous <i>Catoctin Greenstone</i> ANC = 150 - 200 ueq/L
<b>Paine Run</b> SWS Quarterly Chemistry LTEMs, FMP, VDGIF	<b>Staunton River</b> SWS Quarterly Chemistry LTEMs, FMP, VDGIF	<b>Piney River</b> SWS Quarterly Chemistry LTEMs, FMP, VDGIF
<b>Meadow Run</b> SWS Quarterly Chemistry Non-LTEMs, FMP, VDGIF	<b>Brokenback Run</b> SWS Quarterly Chemistry Non-LTEMs, FMP, VDGIF	<b>North Fork Thornton</b> SWS Quarterly Chemistry Non-LTEMs, VDGIF
<b>Twomile Run</b> SWS Quarterly Chemistry LTEMs, FMP, VDGIF	<b>Hazel River</b> SWS Quarterly Chemistry LTEMs, FMP, VDGIF Trout Problem	<b>Jeremy's Run</b> SWS Quarterly Chemistry LTEMs, FMP, VDGIF
<b>Deep Run</b> SWS Quarterly Chemistry Non-LTEMs Drought Stressed Access Problem	<b>North Fork Dry Run</b> SWS Quarterly Chemistry LTEMs Meteorological Station Discharge, Benthic Biology Lake Downstream	<b>Rose River</b> SWS Quarterly Chemistry LTEMs Habitat Structure Known Disturbance
<b>Madison/White Oak Run</b> SWS Quarterly Chemistry Non-LTEMs		<b>White Oak Canyon</b> SWS Quarterly Chemistry LTEMs Disturbance

Headwaters for all watersheds lie within the boundaries of SNP. The lengths of the portions of these streams that flow within SNP range from five to eight kilometers. The slopes of these catchments are steep. The soils of the region are primarily ultisols and inceptisols. Soils within the study region are shallow and rocky, with occasional bedrock exposure. Forest cover is nearly complete. The forests are predominately second growth mixed-deciduous. Air temperature, number of frost-free days, and annual precipitation amounts are fairly uniform across the study region (Cosby et al., 1991).

#### *Stream selection.*

To select the study streams, a matrix of streams and their relevant attributes was used. It first formed a worksheet for the selection of the intensive sites; after the intensive streams were picked, this selection matrix became a worksheet for the selection of the "extensive streams" called for in the proposal (Table 1-2). The intensive streams were selected largely by a process of elimination after stratifying the candidate streams into three ANC categories (LOW, MED and HIGH, defined for this project). The goal was to select one intensive stream in each ANC category. The rows of the selection matrix (Table 1-2) are the streams; rows are blocked by the three ANC categories. Candidate streams were those SNP streams which had the most historical information either on ecology or chemistry or both. The column heads are defined below. The process involved filling in the cells until a stream was eliminated; thus not all cells needed to be filled. The worksheet was filled in by the project team, including also SNP personnel (Julie Thomas, Tom Blount and Dave Haskell).

The last column (Table 1-2, "notes") contains remarks on the overall suitability of the streams as research sites. "Human use" refers to recreational use by park visitors, and is some measure of disturbance and potential for vandalism; three streams were deemed unsuitable for the instrumentation and bioassay work which would take place at the intensive sites. "Trout Problem" refers to unexplained low trout density in the Hazel River, which might result from local poaching; this stream was eliminated for the potential confounding effect it might have on fish community analysis. "Campground" refers to a campground which drains into the Rose River; this might affect stream chemistry. "Small stream" refers to three streams which might not have sufficient habitat diversity to have a perennial, stable fish community; these characteristics were deemed necessary by the project team for streams in

**Table 1-2.** Selection matrix for study streams (see text for explanation). The three intensive streams are marked I\*; the extensive streams are marked E; the SWAS-FMP streams are marked with S; streams marked with X were not included in the study.

Streams		ANC Class	ANC ueq/L	pH	Gageable	Access
Paine Run	I*	Low	8	5.80	Gaged	Good
Meadow Run	E	Low	0	5.44	Poor	Good
Twomile Run	E	Low	16	5.97	Mod	Mod
Deep Run	X	Low		5.55	Mod	Poor
White Oak Run	E	Low	35	6.10	Gaged	Good
Staunton River	I*	Med	89	6.68	Gaged	Good
Brokenback Run	E	Med	92	6.67	Poor	Good
Hazel River	S	Med				
N. Fork Dry Run	E	Med	63	6.42	Gaged	Good
Piney River	I*	High	239	7.01	Gaged	Good
N.F. Thornton	S	High	286	7.08	Good	
Jeremys Run	S	High				
Rose River	S	High	147	6.84	Poor	
White Oak Canyon	S	High	149	6.67		

Streams		Drought Stress	Habitat Quality	LTEMS Site	Chem Freq	Notes
Paine Run	I*	Mod	Good	Yes	Week	
Meadow Run	E	Mod	Poor	No	Qtr	
Twomile Run	E	Mod	Med	Yes	Qtr	Human Use
Deep Run	X	High	?	No	Week	Small stream
White Oak Run	E	High	?	No	Week	Small stream
Staunton River	I*	Low	GOod	Yes	Wek	
Brokenback Run	E	Low	?	No	Qtr	Human Use
Hazel River	S		Poor	Yes	Qtr	Trout Problem
N. Fork Dry Run	E	Mod	?	Yes	Week	Small stream
Piney River	I*	Low	Good	Yes	Week	
N.F. Thornton	S	High		No	Qtr	
Jeremys Run	S			Yes	Qtr	Large stream
Rose River	S			Yes	Qtr	Campground
White Oak Canyon	S			Yes	Qtr	Human Use

which bioassays would be done (the intensive streams), since fish would be drawn from the local stream for study. "Large stream" refers to one stream for which it would be impractical to accomplish the required habitat and fish community surveys in a time frame comparable to the other candidate streams.

In the low ANC category, all but Paine and Meadow were eliminated for reasons in the "notes column"; Meadow was not easily gaugeable, had poor habitat quality in the downstream section where the bioassays needed to be done, and no SNP aquatic LTEMs (Long-Term Ecological Monitoring System) station, leaving Paine.

All streams in the intermediate ANC category were disqualified for reasons in the "notes" column, except Staunton, which fortunately was gaugeable, had good access and an SNP LTEMs station. All but Piney and North Fork of the Thornton (high ANC category) were eliminated for reasons in the "notes" column. N.F. Thornton was eliminated because it regularly experiences drought stress. Fortunately, Piney is adequately gaugeable, and has an LTEMs station.

The other column heads in Table 1-2 are defined here. The first two column heads are ANC category and mean ANC in  $\mu\text{eq/L}$ . The next is mean pH. The next column is a judgment of whether the stream could be effectively gauged using natural controls on water flow, i.e. without building weirs. The next three columns refer to the ease of access to the stream, the extent of drought stress the stream experiences, and a judgment of the quality of habitat for fish the stream provides. The next column records the presence of an SNP LTEMs (long-term ecological monitoring system) station on the stream. The next column ("Chem freq") records how often the stream was sampled before the project, either quarterly (QT), weekly (WK).

#### Intensive streams.

The three streams selected for intensive study are Paine Run, in the lowest ANC category, Piney River in the highest ANC category, and Staunton River in the intermediate ANC category (Tables 1-2 and 1-3). The three catchments associated with the intensive streams are roughly equal in surface area (see Table 1-3 for comparative physical and vegetative characteristics), and all have a mean width of about 4 m. Catchment boundaries and stream routing for each site are shown in Figure 1-1. Maps of the stream synoptic sampling sites,

vegetative cover and geological setting for each catchment are included in Appendix I of this volume.

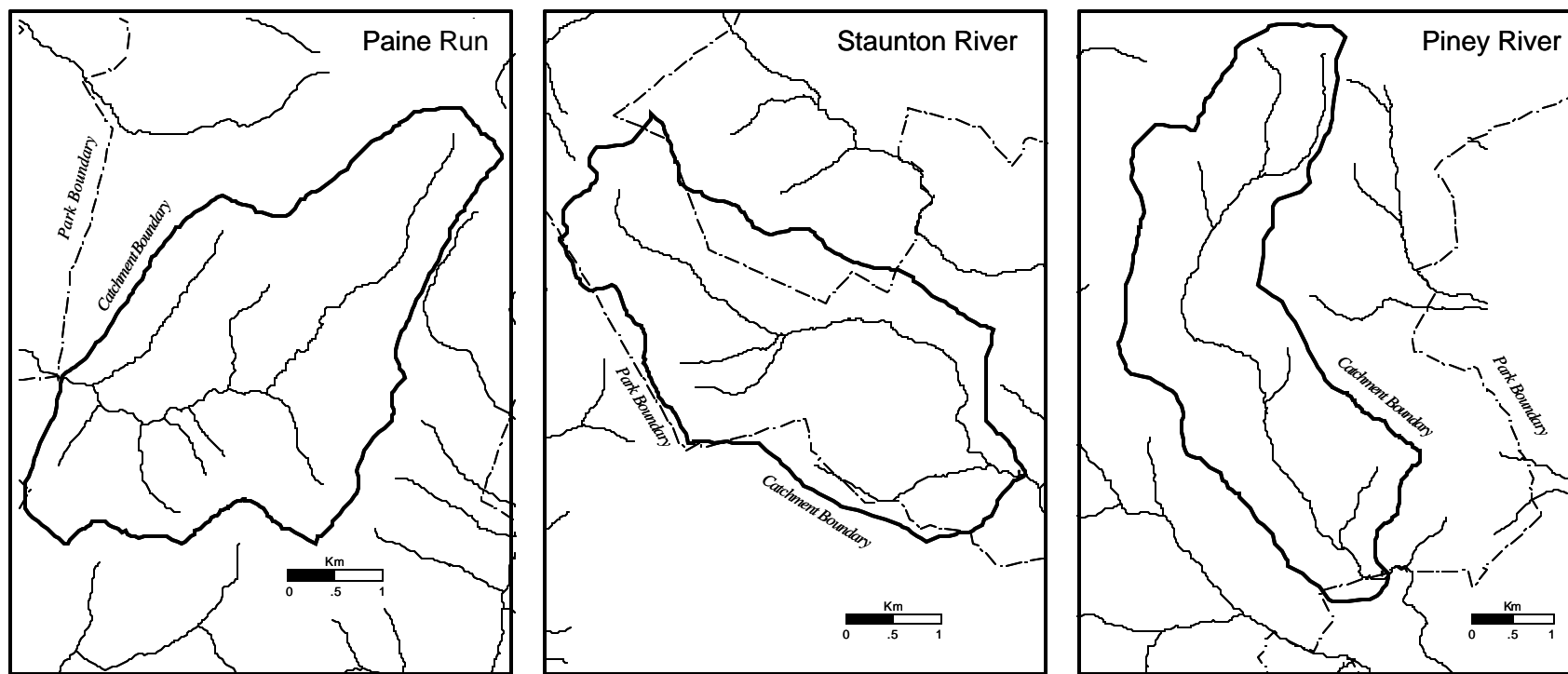
**Table 1-3.** Characteristics of the Intensive Streams.

	<b>Paine Run</b>	<b>Staunton River</b>	<b>Piney River</b>
Sensitivity to Acidification	High	Moderate	Low
Area (km <sup>2</sup> )	12.71	10.56	12.66
Catchment Aspect	Western	Eastern	Western
SNP District	South	Central	North
Major Bedrock Type	Siliciclastic	Granitic	Basaltic
Bedrock Geology	91% <i>Hampton</i> 9% <i>Antietam</i>	82% <i>Pedlar</i> 4% <i>Old Ragg</i>	68% <i>Catoctin</i> 31% <i>Pedlar</i>
Vegetation Classification	96% CO/P 2% H/YP/CH	48% CO/P 11% RO/BL 37% H/P/CH	36% CO/P 18% RO/BL 42% H/YP/CH
Instrument Shed Site Elevation (m)	424	308	347

Paine Run (SNP southern district) exits SNP approximately 6.7 km southeast of the town of Grottoes (Augusta county). Paine Run is underlain by silici-clastic rock and is extremely sensitive to acidification (ANC < 25 ueq/L). Paine Run flows west from an elevation of about 730 m to its confluence with the South River.

Staunton River (SNP central district) exits SNP approximately 1.4 km northwest of Graves Mill (Madison county). It is underlain by granitic rock and is intermediate in sensitivity (ANC 60-100 ueq/L). Staunton River flows east from an elevation of about 960 m to its confluence with the Rapidan River.

Piney River (SNP northern district) exits SNP approximately 5.7 miles northwest of Sperryville (Rappahannock county). Piney River is underlain by basaltic rock and is the least sensitive to acidification (ANC 150-250 ueq/L). Piney River flows east from about 970 m elevation to its confluence with the North Fork of the Thornton River.



**Figure 1-1.** The catchment boundaries and stream routing of the three intensive study sites in the SNP:FISH Project.

Extensive streams.

The proposal calls for additional streams to provide information on potential acidic deposition effects on a somewhat wider geographic scale ("extensive sites"), and sampled less frequently. The project team, including Tom Blount and Julie Thomas of SNP, decided to use the extensive sites to gather more information on sensitive and intermediate sites, and to exclude additional higher-ANC sites where acidic deposition effects are less likely. One of us, Keith Eshleman, has diverse experience in acidic deposition monitoring of streams, and has indicated that some acidification projects have used too many resources on insensitive streams in the service of a balanced experimental design. Since the focus of the proposal is the detection of acidic deposition effects, it seemed unwise to use our resources on too many streams where effects are unlikely. As a result, we identified three extensive streams in the low ANC category, and two in the intermediate category (Table 1-2).

The criteria for selection of extensive sites did not need to be as stringent as for intensive sites. Since these streams would neither be gauged nor used for bioassays, gaugability and heavy use by visitors (i.e., potential for vandalism) are not issues; neither is small size. Indeed, small size may provide valuable information about the scaling of hydrochemical responsiveness. Ideally, these streams should have an LTEMs site, good access, low drought stress and good fish habitat. Unfortunately, most of the candidate streams do not meet all these requirements. However, White Oak Run and North Fork Dry Run have a history of weekly sampling (through SWAS, Shenandoah Watershed Study), as well as soils information which may prove valuable; both are also gauged.

SWAS-FMP streams.

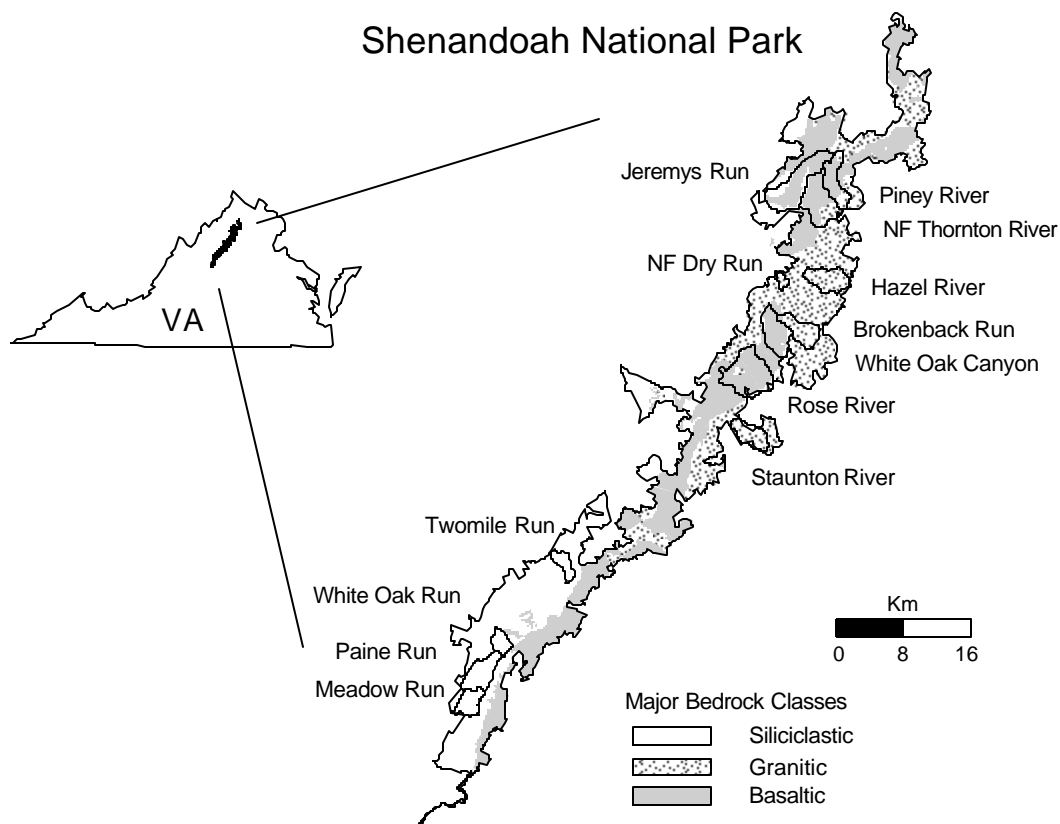
In addition to the three "intensive" streams (Paine, Staunton, Piney) and five "extensive" streams (Meadow, Twomile, White Oak, Brokenback, North Fork Dry) quarterly stream chemistry from the UVA's SWAS program plus fish community surveys from the Shenandoah National Park's Fisheries Management Program (FMP) were also available for five streams; these data were incorporated into the relationship between stream ANC and fish species richness discussed in Chapter 6C. These five streams (Hazel, White Oak Canyon, Jeremy's, Rose, North Fork Thornton) are grouped as the "SWAS-FMP" streams (Table 1-4). The reason for their inclusion was that quarterly chemistry for at least seven years for each was on hand, and reliable



fish community surveys had been performed by SNP staff; thus they met the criteria for inclusion in the regression models for species richness and ANC, and they also provided the opportunity to include higher ANC streams in this that analysis.

**Table 1-4.** The final list of study streams in the SNP:FISH project.

Intensive Streams	Extensive Streams	SWAS-FMP Streams
Paine Run	Meadow Run	Hazel River
Staunton River	Twomile Run	White Oak Canyon
Piney River	White Oak Run	Jeremy's Run
	Brokenback Run	Rose River
	North Fork Dry Run	North Fork Thornton River



**Figure1-2.** The location of the SNP:FISH study streams and their associated geologic setting.

## Summary of Results

The "Shenandoah National Park: Fish in Sensitive Habitats" project was a response to the finding that there had been a significant decline in the pH and acid neutralizing capacity in Shenandoah National Park (SNP) streams between 1979 and 1991. The project was begun in 1992. The overall purposes of the SNP:FISH project were to assess the potential impact of acidification on fish populations in Shenandoah National Park (SNP), and to predict likely future effects based on current relationships between water chemistry and fish responses.

The orientation of the project is an integrated, multidisciplinary analysis of chemical/biotic linkages in the context of acidification effects. The advantages of this integrated approach are that the linkages among geology, hydrology, water chemistry, aquatic chemistry, habitat structure, and biotic responses can be assessed simultaneously, and at the same locations.

The advantages in using fishes as indicators of acidification are as follows. 1) Fishes are a valuable resource, and the historical composition of fish communities is relatively well known for many streams. 2) The mechanisms of acidification effects on fish are direct and unambiguous: both elevated hydrogen ion (low pH) and aluminum (mobilized by acidification) are toxic to fish.

The strategy of the project is to build on existing monitoring and research programs (SNP:Long Term Ecological Monitoring System, Fisheries Management Plan; UVA: Shenandoah Watershed Study) while adding new components designed to detect biotic responses to acidification.

The product of this effort is a research and assessment document including techniques to detect acidification impacts on SNP fish communities, in addition to an evaluation of current effects. Predictive models of fish response have also been produced to estimate impacts under changing acidification scenarios.

The principal scientific results of the project are presented in detail in the individual chapters of this and the companion volumes of this report. This summary of results gives a chapter-by-chapter synopsis of the results. The reader is also directed to the Executive Summary at the beginning of this chapter.

## **Synopsis of Chapter 1: Project Overview and Summary of Results**

### *Acidification*

"Acid Rain" implies the deposition of acid materials as wet deposition (rain, snow, fog, cloud) as well as dry deposition of particles and gases. Scientists use "acid deposition" for this process, because it explicitly includes both dry and wet deposition; indeed, dry deposition of acid materials is often equal to the amount deposited in wet form. Acid deposition is responsible for the loss of hundreds of fish populations in Europe and North America.

### *Acid deposition effects on fish.*

The effects of acid deposition on fish involve processes operating at different spatial scales. Nevertheless, the interaction of these processes can be summarized in an outline consisting of five major points.

- 1) The source of the acid: fossil fuel combustion.
- 2) Landscapes differ in acid-sensitivity, based on geology and soils.
- 3) The role of aluminum: metabolic poison mobilized from soils by acid.
- 4) Site of toxic action: fish gill
- 5) The cause of death: circulatory collapse secondary to electrolyte imbalance.

### *Selection of Streams.*

The SNP:FISH proposal study design included three streams to be instrumented for high frequency measurements of discharge, water chemistry (focusing on episodes), plus multiple fish community and habitat surveys, plus bioassays with brook trout and blacknose dace. One stream in each of the major bedrock categories (which yield waters with low, intermediate or high acid neutralizing capacity) in SNP was selected, and the design executed. The design also called for additional streams to provide wider geographic collection of information, but collected less frequently. Three streams in the low-ANC category and two streams in the intermediate ANC category were selected, and the design executed.

## **Synopsis of Chapter 2: Application of Research Findings for Resource Management in Shenandoah National Park Using the MAGIC:FISH model**

The MAGIC model of stream and catchment responses to atmospheric deposition (version 5.01) was modified to include the fish effects established in this project. The modified version of the model was named MAGIC:FISH (version 5.01). The model was then applied to each of the intensively studied sites for which bioassays were performed (Paine Run, Piney Run and Staunton River). The details of the incorporation of the fish responses into MAGIC and the calibration results for the three catchments are described in Chapter 7.

The material in Chapter 2 is intended to provide an overview of the protocol for applying MAGIC:FISH that might be used by SNP management personnel in response to future assessment needs. Copies of the model that can be run on PC computers and the calibrated parameter files for each intensively studied stream are provided on the CD-ROM accompanying this report. Chapter 2 provides:

- 1) a description of the MAGIC model and its prior uses in acid deposition studies;
- 2) a conceptual discussion of the dynamics of acidification as modelled by MAGIC;
- 3) a discussion of the approach taken and the data needed to calibrate the model;
- 4) details of the modeling protocol used for applying MAGIC in the SNP:FISH project, including procedures for data assembly and management, and a description of the output products;
- 5) suggested procedures for providing performance analysis of model calibrations;
- 6) suggested procedures for providing uncertainty estimates of simulated responses to scenario and strategy runs;
- 7) a generalized classification system for linking water quality changes to fish responses abstracted from this project for general use when details of episodic water quality and/or aluminum concentrations in streams are not available.

## **Synopsis of Chapter 3: Synoptic stream-water chemistry.**

The purpose of this component of the FISH project was to define the baseflow geochemical regime of the FISH study watersheds. Specifically, objectives were to determine the spatial and temporal variability in the acid-base status of the streams, and identify landscape characteristics associated with that variability.

Preliminary information on bedrock geology was important from the outset in identifying the project watersheds, so that the study streams could be stratified by acid-base status. The study confirmed the expectation that, within SNP, siliciclastic bedrock yields surface waters with low ANC, granitic bedrock yields streams with intermediate ANC, and basaltic bedrock yields streams with highest ANC, i.e., the bedrock types most resistant to weathering produce streams with the least buffering capacity. Thus a major determinant of spatial variation in acid-base status is bedrock type. ANC values of SNP streams were placed into categories to summarize the likely consequences to the fish community of chronic exposure to those ANC values, as an aid to interpretation of acid-base status effects discussed in this component.

Synoptic surveys at multiple sites upstream of the weekly sampling locations on each stream indicate that ANC and pH values generally decrease in an upstream direction, as in other areas.

The context of temporal variation described in this component relates to seasonal and inter-annual temporal variation; Chapter 4 deals with very short term variation on the scale of days and individual acid episodes.

Cold season (winter and spring) ANC values are typically lower than warm season (summer and fall) ANC values for the same stream, with some exceptions. The lowest within-season values of ANC typically occur during high flow. Thus the lowest ANC and pH values typically occur during cold season high flow conditions, when sensitive young brook trout are in the streams.

Regression models were developed to provide quantitative predictions of baseflow ANC, based on the percentages of catchments underlain by various bedrock types, plus other landscape characteristics. These models have coefficients of determination of 0.84 to 0.94. Bedrock type provides the most explanatory power; two additional landscape variables (watershed area and percent-high-quality forest) provided only about 2% each increase in variance explained.

Model evaluation procedures indicated that the models are good at predicting membership in the low and high fish-viability classes of ANC values, supporting their utility for extrapolation to other watersheds. This is supported also by the strong theoretical and empirical relationships in general between bedrock type and ANC. Thus, there is strong linkage between bedrock type and the stream's fish community.

#### **Synopsis of Chapter 4: Discharge and water chemistry at the three intensive sites.**

Rating curves and discharge hydrographs were developed for each of the intensively monitored streams over the three water years from 1 October 1992 to 30 September 1995 (except for Staunton River, where data are only available through mid-May 1995, due to the massive flood which carried away the field equipment in June 1995).

Estimated long-term mean discharge for the three intensively monitored streams ranges from 443 to 562 mm/yr. Paine Run had the lowest baseflow discharge and highest stormflow discharge of the three streams, making it the "flashiest" of the three.

Stream ANC varied both seasonally and in response to stormflow at all three sites. In Paine, ANC always peaked (15-20  $\mu\text{eq/L}$ ) in late summer/early fall when discharge was lowest; ANC was lowest (0-5  $\mu\text{eq/L}$ ) in late winter/early spring; and significant ANC depressions (25  $\mu\text{eq/L}$ ) occurred in all seasons during stormflow episodes, when ANC reached as low as -9  $\mu\text{eq/L}$ . Late summer peak ANC values were 100-130  $\mu\text{eq/L}$  at Staunton, with winter minima of 30-50  $\mu\text{eq/L}$ , and episodic depressions of 25-75  $\mu\text{eq/L}$ . Peak ANC values were 250-400  $\mu\text{eq/L}$  at Piney, minima were 95-100  $\mu\text{eq/L}$ , with episodic depressions of 75-150  $\mu\text{eq/L}$ . All three streams showed higher concentrations of sulfate in the dormant versus the growing season.

Episodic acidification (transient loss of ANC, and associated pH depression and increase in dissolved toxic aluminum) is ubiquitous and largely hydrologically controlled. The primary acidifying effect in all three catchments results from atmospheric inputs of sulfur; secondary causes were site-specific, and included nitric acid inputs, organic acids, and base cation dilution. The nitric acid inputs during episodes in SNP may result from periodic gypsy moth defoliations starting in the 1980s; episodic acidification may have been intensified by this introduced pest. The organic acid inputs are thought to result from the release of natural humic substances within the catchment.

Streams with low baseflow ANC clearly experience the worst acid episodes. Analysis of 50 baseflow-stormflow pairs, and two-component mixing analysis, showed that pre-episode ANC is an excellent predictor of the minimum ANC during episodes, explaining 90% of the variance in minimum ANC in a bivariate linear regression model. An average of 75% of discharge at peak stormflow is pre-event ("old") water. Relative to two regions well-studied in the context of episodic acidification, the Adirondacks and the Catskills, acid episodes in SNP are

less intense because the ANC of "new" water is less acid. The relationships discovered between baseflow and stormflow ANC in SNP were incorporated into the model described in Chapter 7.

### **Synopsis of Chapter 5A: Influence of water quality and physical habitat on brook trout and blacknose dace in the three intensive streams.**

The primary purpose of this component was to establish linkages between fish density, habitat structure, and water chemistry. It was important from the outset to be able to attribute any differences among the fish communities of the streams appropriately to habitat, biotic interactions or acidification. Techniques for this component were the basinwide visual estimation technique (BVET) for physical habitat, and snorkel diving plus multiple-pass removal (electroshocking) for the fish surveys. Water chemistry data were derived from synoptic surveys described in Chapter 3.

Habitat was surveyed in over 10 km of stream length (main branch plus tributaries) available to fish (wetted habitat) in each of the three watersheds. Total surface area of wetted habitat was similar among all three streams (from 24,892 m<sup>2</sup> in Paine, to 28,056 m<sup>2</sup> in Piney). In total, Paine had 453 pools and 402 riffles; Staunton had 398 pools and 185 riffles, and Piney had 313 pools and 289 riffles. Number of fish species increased with ANC from 3 species in Paine, to 5 in Staunton, to 7 in Piney.

Only brook trout and blacknose dace occurred in all three streams, so quantitative comparisons were limited to these two species. Densities of both species were lower in riffles versus pools, and densities in riffles did not differ across streams. Detailed comparisons of densities across the three streams will therefore focus on the significant differences in densities in pool habitat units.

Density of brook trout in pools was 13 trout/100m<sup>2</sup> of stream surface area in Paine, versus 25/100m<sup>2</sup> in Staunton, and 41/100m<sup>2</sup> in Piney. Trout density increased significantly with increasing ANC and pH. Statistical analysis (Principal Components Analysis) indicated that no combination of habitat characteristics explained the variance in trout density across streams, whereas water chemistry plus habitat did.

In contrast to brook trout, patterns in dace densities appear to be influenced conspicuously by fish community structure as well as by physical/chemical differences across streams. Blacknose dace density was similar in Piney (high ANC) and Paine (low ANC), at 22

and 23 dace/100m<sup>2</sup>, respectively, versus only 6 dace/100m<sup>2</sup> in Staunton. It should be noted, however, that density estimates for blacknose dace in the three intensive streams are all low compared to the five extensive streams. In brief, blacknose dace densities appear to be limited by biotic interactions (competition and/or predation) in Staunton and Piney, where more fish species are present, and by acidification stress in Paine Run.

The effect of ANC and pH on brook trout density is not unexpected, given the demonstrated sensitivity of early life stages to acidification in poorly buffered streams (Chapter 6). The absence of a ubiquitous acidification effect in blacknose dace may result from life history differences with respect to trout: blacknose dace breed in summer when SNP streams are at peak ANC. Young dace are temporally isolated from the worst acid episodes, which are coincident with the presence of trout early life stages in fall, winter, and spring. Adult blacknose dace can tolerate acid episodes which kill trout embryos (Chapter 6).

#### **Synopsis of Chapter 5B: Condition, production, and population dynamics of brook trout and blacknose dace in the three intensive streams.**

The primary objective of this component was to examine the relative performance of fish populations among the three intensive streams and to infer the relationship between fish performance and water quality. The patterns which emerged relating the responses of various age classes and species were complex, and are summarized below, first for trout, then for blacknose dace.

*Trout: condition factor (K), mean weight and density.*

The mean weights of trout from Piney and Staunton (high and intermediate ANC streams, respectively) were similar, and significantly heavier than trout from the low-ANC stream (Paine). The condition factors of trout from Paine and Piney were similar, and significantly lower than trout from Staunton.

For Paine Run (low ANC), the combination of poor condition plus low mean weight suggests that poor water quality may limit trout growth. It does not appear that competition is limiting growth: density of trout was always lower in Paine versus Piney.

Density of trout was highest in Piney (high ANC) during all four surveys; trout density was similar in Staunton and Paine in two surveys, higher in Paine versus Staunton in one survey, and lower in Paine versus Staunton in one survey.



The confidence intervals for trout annual production (kg/100m<sup>2</sup>) in the three streams are non-overlapping: 24-26 kg/ha in Paine, 28-40 kg/ha in Staunton, and 48-77 kg/ha in Piney. Nevertheless, trout annual production was not significantly different among the streams.

*Blacknose dace: condition factor (K), mean weight, and density.*

The most significant differences which emerged for blacknose dace were also condition factor (K), mean weight, and density. Paine (low ANC) always had the lowest mean weight and K, versus Piney and Staunton which were similar to each other and higher for both variables. Of the three intensive streams, density of dace was highest in Paine Run, the low-ANC stream. It should be noted, however, that all density estimates for blacknose dace in the intensive streams are relatively low, for reasons discussed in the Executive Summary.

#### **Synopsis of Chapter 5C: Response of brook trout and blacknose dace to acidification in a laboratory stream.**

The objectives of this component were to determine the ability of the two species (in separate experiments) to avoid depressions in ambient pH, and to recognize and use a pH-neutral microhabitat available in the experimental stream at Virginia Tech. Both species clearly avoided the acid pulse (ambient pH lowered from 7.2 to 5.1) and sheltered in the pH-neutral refuge. Availability of food did not deter fish from leaving the experimental channel after it was acidified. The pH of the acid pulse was less severe than that observed in Paine Run during acid episodes, so it was not unrealistic. In nature, tributaries such as Paine's Lefthand Hollow, which has significantly higher ANC than the main stem, may offer refuge to Paine Run fish during episodes.

#### **Synopsis of Chapter 5D: Inventory of physical habitat and fish populations in the five extensive streams.**

Three additional streams with low baseflow ANC (White Oak Run, Twomile Run, Meadow Run) and two additional streams with intermediate baseflow ANC (Brokenback Run, Shaver Hollow ) were surveyed using the same techniques as for the intensively studied streams to gain a broader geographic reference for conclusions about potential acidification and habitat effects than provided by the intensively studied streams, Paine Run (low ANC), Staunton River (intermediate ANC) and Piney River (high ANC). The design included more streams in the

more sensitive categories to maximize sampling effort in streams where acidification effects were more likely. Data on aquatic habitats, and trout and dace populations are summarized in Chapter 5D Tables 5D-1 and 5D-2.

Fish species present in the three low-ANC extensive streams were:

White Oak Run (3): brook trout, blacknose dace, fantail darter;

Twomile Run (2): brook trout, blacknose dace; and

Meadow Run (2): brook trout (blacknose dace recently lost).

Fish species present in the two mid-ANC extensive streams were:

Shaver Hollow(NF Dry Run) (2): brook trout, blacknose dace; and

Brokenback Run (3): brook trout, blacknose dace, eel.

### **Synopsis of Chapter 6A: Susceptibility of young brook trout and adult blacknose dace to acidification.**

This chapter (6A) provides a brief history of studies of acidification effects on fish, and an explanation of the toxic mechanisms of low pH and aluminum, including the ameliorating effects of environmental calcium. The low calcium concentration of some SNP streams accounts for the higher mortality at any given pH/aluminum concentration than seen in other locations where calcium is higher.

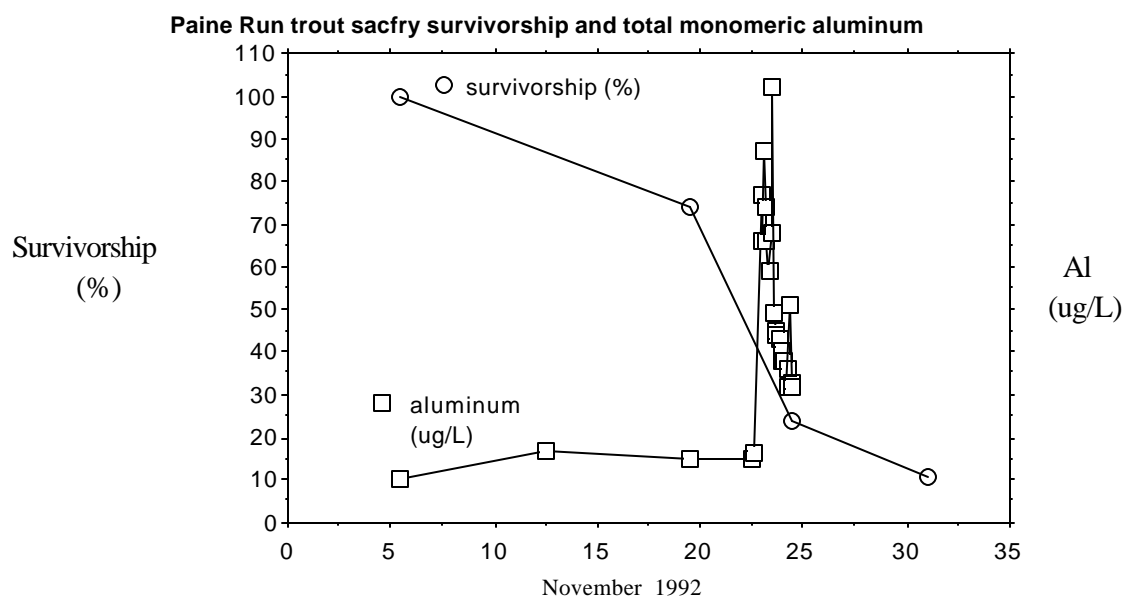
The objectives of this component of the project were to assess the potential effects of chronic and episodic acidification on a) early life stages of trout, and b) adult blacknose dace. Effects were evaluated using in situ bioassays in the three intensively studied streams: Paine Run (low-ANC), Staunton River (intermediate-ANC) and Piney River (high-ANC).

Lethality of baseflow and acid episodes in SNP were evaluated with eggs and fry of brook trout placed in artificial nests so that they could be easily inspected and counted. Live, healthy eggs (1000-2000 per stream per bioassay) from hatcheries were included in 3 fall, and 3 spring bioassays. In brook trout, as in other fish species, young fish are more sensitive to acid/aluminum stress than adults.

Three major sources of mortality were identified: flood and sedimentation (high mortality following storm flows which mechanically damaged the young fish and/or clogged the gravel nests with silt); drought (high mortality in all three streams due to fungal infection secondary to low water flow through the gravel nests); and acidification (3 out of 6 bioassays).

In each of the three bioassays showing acidification effects, trout in Piney River (high-ANC) showed higher survival rates than trout in Paine Run (low-ANC). Survival at Staunton River (intermediate ANC) varied among bioassays. Episodic versus chronic acidification effects could be distinguished; mortality immediately following stormflow with low-pH/high-aluminum concentrations occurred in 2 out of 6 bioassays, and mortality associated with chronic acidification occurred in 1 out of 6 bioassays.

The relationship discovered between trout fry mortality and acid aluminum concentration during episodes was incorporated into the predictive model described in Chapter 7. This is illustrated below (Figure 1-3) with data from an individual episode.



**Figure 1-3.** Relationship between trout fry survival and dissolved aluminum during an acid episode in an SNP stream (Paine Run).

The algorithm based on this and similar responses is such that trout fry mortality is 0% at 20 $\mu$ g/L Al, and 100% at 80 $\mu$ g/L and above during episodes. Survivorship is assumed to be linearly related to aluminum concentration between 20 and 80  $\mu$ g/L. It should be noted that 80 $\mu$ g/L may not produce 100% mortality in streams which have higher calcium concentrations than characteristic of low-ANC streams in SNP; for example, baseflow calcium in Paine Run is about 30  $\mu$ eq/L, or about 0.5 mg/L calcium, a very low value.

### *Blacknose dace bioassays.*

Adult blacknose dace did not exhibit either lethal, or sublethal acid/aluminum stress as measured by hematocrit, under chronic (as opposed to acid episodes) field conditions; episode responses were not measured. Blacknose dace did, however, demonstrate chronic sublethal acidification effects in terms of condition factor (K) (Chapter 6B).

Brook trout adults are regarded as more tolerant of acidification effects than blacknose dace adults; in both species the young are regarded as more sensitive than adults. Yet this study has shown that brook trout young can be more sensitive than blacknose dace adults: during the fall 1994 bioassay in Paine Run, significant mortality occurred among brook trout fry, while simultaneously, blacknose dace showed 100% survival. In the early stages of acidification, when through reproductive timing, blacknose dace young are isolated from the worst acid events and survive, there may already be negative effects on brook trout young. Thus, the presence of the more sensitive species (blacknose dace) does not mean that the more tolerant species (brook trout) is still unaffected.

### **Synopsis of Chapter 6B: The susceptibility of blacknose dace (*Rhinichthys atratulus*) to acidification.**

This chapter (6B) provides background on the vulnerability of the fish community in SNP to acidification. The "critical pH" (the pH at which negative effects of acidification are likely at the population level) is known for 9 of the 28 fish species in SNP; pH values below the critical pH for all nine species have been recorded in low-ANC SNP streams. Blacknose dace in SNP currently experience acidification conditions associated with deleterious effects in the Adirondack Mountains and Ontario.

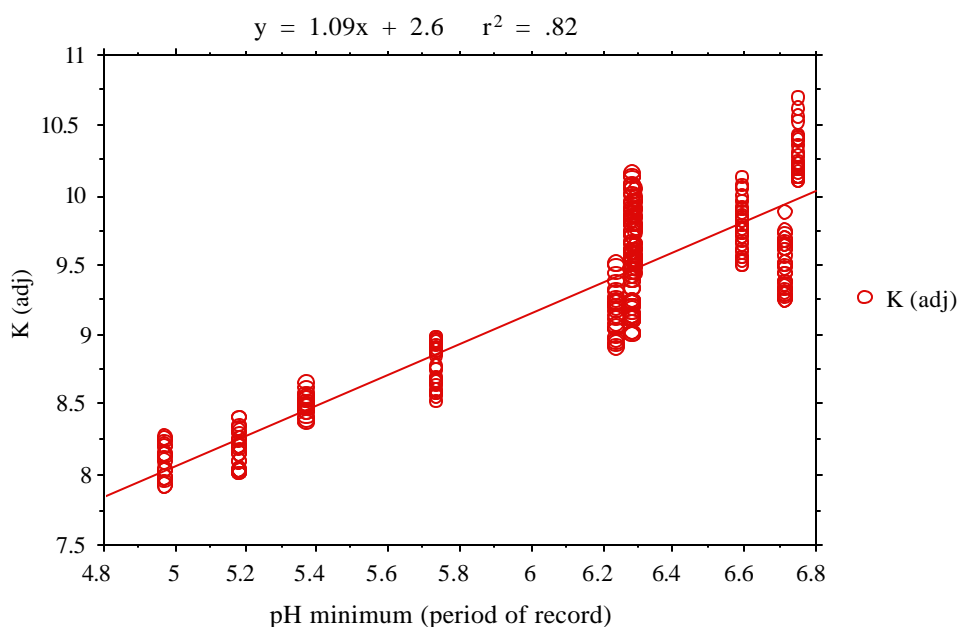
This chapter provides a description of aluminum chemistry and the relationship between pH and aluminum toxicity.

Bioassays using adult blacknose dace did not reveal sublethal acidification effects as measured by the whole-body-sodium technique (WBNa), one measure of sublethal acidification stress. However, both bioassays and population surveys showed a strong relationship between stream acid-base status and condition factor (another indicator of sublethal stress). Repeated surveys measuring length and weight of more than 1200 dace showed perennial differences among blacknose dace from different streams, such that fish from low-ANC streams are lighter

and shorter than fish from mid-ANC and high-ANC streams. These results suggest that dace may currently compensate for sublethal acid stress at the expense of maximum growth. These data also revealed a seasonal pattern in dace condition factor, indicating that comparisons of condition factor must be made between samples of fish collected and measured at the same season.

The relationship between water quality and blacknose dace condition factor was expanded to include the 5 "extensive" streams. Nearly simultaneous sampling in all 8 streams avoided demonstrated seasonal effects on K. Sampling time in the last week of July, 1994, permitted the inclusion of three more streams for which water quality data were available, so the relationship reported here is based on 11 streams.

The relationship discovered between blacknose dace condition factor and stream pH was incorporated into the predictive model described in Chapter 7. This is illustrated below (Figure 1-4) with the regression equation incorporated into the model, and the data from the eleven streams, representing measurements of more than 300 fish.

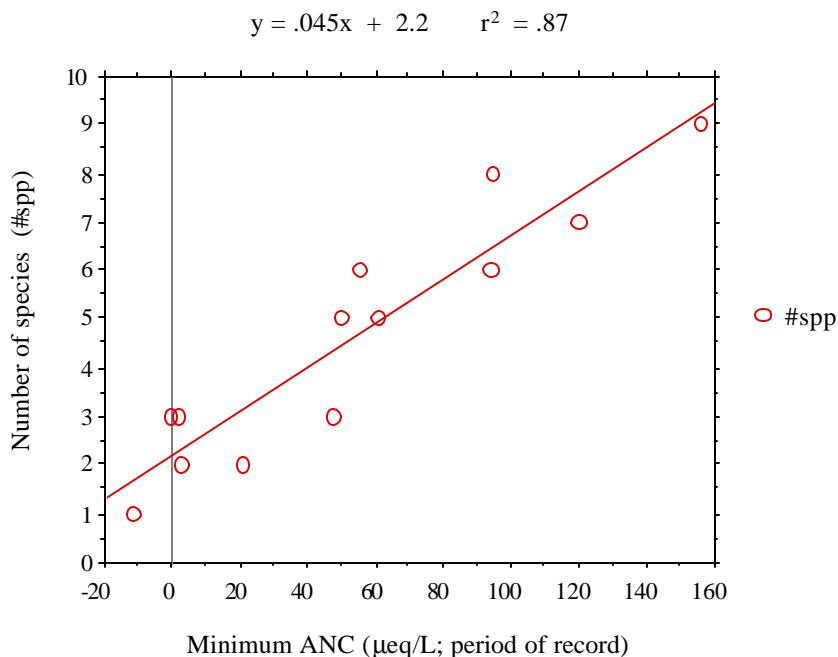


**Figure 1-4.** Relationship between condition factor (K, adjusted for length covariance) of blacknose dace and Minimum pH (recorded over the previous three years) in SNP streams.

## Synopsis of Chapter 6C: Relationship between acid-base status and number of fish species in SNP streams.

The purpose of this component of the FISH project is to determine the relationship between fish species richness and acid-base status of streams. Acidification has been shown to reduce fish species richness by eliminating sensitive species. The streams used in this analysis include the three FISH intensive sites (Paine, Staunton and Piney), the five extensive sites (Meadow, Twomile, White Oak, Brokenback, and North Fork Dry) plus other streams for which long-term records of stream chemistry and fish collections exist, for a total of 13 streams.

A stepwise multiple regression was performed, using fish species richness as the dependent variable, and the median, minimum, and maximum values for each of the water chemistry values as potential predictor variables. The period of record for both chemistry and fish species number was at least 7 years for all streams. There was a highly significant ( $p < 0.0001$ ) relationship between minimum ANC (over the period of record) and fish species richness, such that streams with the lowest ANC values had the fewest fish species. Minimum ANC alone accounted for 89% of the variance in fish species richness, so the results are presented for this variable alone (Figure 1-5).



**Figure 1-5.** Relationship between number of fish species (#spp) and Minimum ANC recorded in SNP streams; data derived from SNP Fisheries Management Plan (FMP) and the FISH project.

## **Synopsis of Chapter 7: Modelling the biological effects of water quality changes in the three intensive streams.**

The objective of this component of the project was to incorporate the relationships between water chemistry and fish responses described in Chapter 6 into an interactive computer simulation model. This will allow users to predict likely fish community responses to changing acidification scenarios in the future, as well as to reconstruct the pre-acidification acid-base status of SNP streams and their fish communities.

The simulation framework is based on the catchment-scale model MAGIC. The MAGIC model uses soil chemistry and precipitation chemistry to predict stream chemistry. It has been modified for the SNP:FISH project to simulate acid episodes with short-term fish responses, and use the standard "baseflow" outputs of MAGIC to simulate longer-term response of the fish community. The three fish response functions derived from the relationships between fish and chemistry in Chapters 6A, 6B, and 6C were incorporated into the model.

MAGIC has been widely used and tested. In particular, MAGIC was the principal model used by the National Acid Precipitation Assessment Program (NAPAP) to estimate the potential future damage to lakes and streams in the eastern United States. It has been used also to predict brown trout responses in Norway and Scotland, based on simple "baseflow" ANC outputs.

In addition to the modified model itself as a product for SNP use, three scenarios of future acidic deposition were performed: constant sulfate deposition at 1994 levels, and two levels of reduced deposition (40% and 70% reductions from 1994 levels). For each scenario, simulations were run for fifty years into the future (1994 to 2044). For the two scenarios assuming reduced deposition, the sulfate deposition was reduced linearly over 20 years (1994 - 2014), with constant sulfate deposition at the reduced level for the final 30 years of simulation (2014 - 2044). Output from the future simulations are examined at two times, the years 2015 and 2044. The forecasts suggest that future water quality in these three streams will not improve under any of the three simulation scenarios (Chapter 7, Figs. 7-4 A,B&C). The outlook for Paine Run is the poorest. For both constant and 40% deposition reductions, large losses of ANC are forecast for this stream. In fact, these two scenarios produce chronic acidity in Paine Run within 20 years. The simulation results suggest that a 70% reduction in deposition is necessary to maintain the current baseflow water quality in Paine Run. However, even a 70% reduction will not eliminate episodic acidification in response to intense storms in Paine Run.

Under projected conditions of chronic acidity (under a 40% reduction), it is virtually certain that the blacknose dace population of Paine will disappear (as well as the blacknose dace populations of streams with similar or lower ANC in the Park); conditions lethal to brook trout fry are expected to occur commonly. Based on comparisons to other brook trout populations described in Chapter 5, if a marginal Paine Run brook trout population survives, it can be expected to show even lower density and/or poorer condition factor than at present. Thus we predict that SNP will lose fish populations even under a 40% reduction in acid inputs.

### **Project Summary**

Our research in forested headwater catchments in the Shenandoah National Park, VA, has demonstrated that both chronic and episodic acidification occur in streams in the region. Our studies have also shown that changes in water quality accompanying acidification are related to observable biogeochemical characteristics of the landscape. The susceptibility of streams to acidification is largely geologically determined and empirical relationships can be used to classify sensitive landscape types. Rates of acidification are moderated by forest and soil biogeochemical processes and can be projected using the process-based MAGIC model. The effects of stream acidification on fish are documented in this report for the first time for streams in the Shenandoah National Park (SNP), VA. These effects can be observed at different ecosystem levels and can be quantified using empirical and process-based models:

- 1) community-level effects (reduced species richness in streams);
- 2) population-level effects (increased mortality of brook trout, *Salvelinus fontinalis*);
- 3) effects on single organisms (reduced condition factor of individuals).

Based on these results, we can now link water-quality changes to adverse effects (both lethal and sub-lethal) on fish in SNP streams. These linkages provide a unique resource with which we can construct conceptual and mathematical models that have both scientific and management utility; models that can aid our understanding of the complex interactions in the stream ecosystems and can quantify expected responses. The results of this study (and the computer model linking the chain of effects) provide the capability for park managers to incorporate acidification effects on fish as one component in any integrated analyses of the past, current, and future responses to acidic deposition of aquatic resources in the park.



## References

- Altshuller, A.P., and Linthurst, R.A. 1984. The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers. EPA/600/8-83/016BF. U.S. Environmental Protection Agency, Washington, D.C.
- Baker, L.A., Kaufmann, P.R., Herlihy, A.T., and Eilers, J.M. 1991. "Acid Lakes and Streams in the United States: the Role of Acidic Deposition", *Science*, 252, 1151-1154.
- Cosby, B.J., Ryan, P.F., Webb, J.R., Hornberger, G.M., and Galloway J.N. 1991. In D.F. Charles, ed. *Acidic Deposition and Aquatic Ecosystems*. Springer-Verlag, New York, p.297-318.
- Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N. 1985. "Modeling the Effects of Acid Deposition: Estimation of Long-Term Water Quality Responses in a Small Forested Catchment", *Water Resources Research*, 21, 591-1601.
- Gathright, T.M. 1976. *Geology of Shenandoah National Park, Virginia*. Bull. 86, 93 pp., Va. Div. of Mineral Resources.
- Gibson, J.H., Galloway, J.N., Schofield, C., McFee, W., Johnson, S., McCarely, S., Dise, N., and Herzog, D. 1983. *Rocky Mountain Acidification Study*. U.S. Fish and Wildlife Service, Division of Biological Services, Eastern Energy and Land Use Team, FWS/OBS-8-/40.17.
- Hendrey, G.R., Galloway, J.N., Norton, S.A., Schofield, C.L., Shaffer, P.W. and Burns D.A. 1980. *Geological and Hydrochemical Sensitivity of the Eastern United States to Acid Precipitation*, U.S. Environmental Protection Agency, EPA-600/3-80-024.
- Herlihy, A.T., Kaufmann, P.R., Church, M.R., Wigington, P.J., Webb, J.R. and Sale, M.J. 1993. "The Effects of Acidic Deposition on Streams in the Appalachian Mountain and Piedmont Region of the Mid-Atlantic United States", *Water Resources Research*, 29: 2687-2703.
- Knapp, C.M., Heimbuch, D.G., Greening, H.S., and Filbin G.J. 1988. *Maryland Synoptic Stream Survey*. Prepared by International Science and Technology, Inc. for the Maryland Dept. of Natural Resource, Power Plant Research Program. Annapolis, MD. AD-88-2.
- Lynch, D.D. and Dise, N.B. 1985, *Sensitivity of Stream Basins in Shenandoah National Park to Acid Deposition*,. U.S. Geological Survey, Water-Resources Investigations Report, 85-4115. NADP/NTN 1986-1991.
- National Atmospheric Deposition Program (IR-7) /National Trends Network. March 8, 1989. NADP/NTN Coordination Office, Natural Resources Ecology Laboratory, Colorado State University, Fort Collins, CO 80523.

- Schindler, D.W., Mills, K.H., Malley, D.F., Findlay, D.L., Shearer, J.A., Davies, I.J., Turner, M.A., Linsey, G.A., and Cruikshank, D.R. 1985. Long-term ecosystem stress: The effects of years of experimental acidification on a small lake. *Science*. 288:1395-1401.
- Webb, J.R., Cosby, B.J., Galloway, J.N. and Hornberger, G.M. 1989. Acidification of native brook trout streams in Virginia. *Water Resources Research*, 25:1367-1377.
- Winger, P., Lasier, P.J., Hurdy, M., Fowler, D., and Van Den Avyle, M.J. 1987. Sensitivity of high-elevation streams in the Southern Blue Ridge Province to acidic deposition, *Water Resour. Bull.* 23:379-386.

**SNP:FISH**  
**Shenandoah National Park: Fish In Sensitive Habitats**  
**Project Final Report, Volume I**

**Chapter 2**  
**Application of Research Findings for Resource Management**  
**in Shenandoah National Park Using the MAGIC:FISH model**

**Prepared by**  
**B.J. Cosby**  
**Department of Environmental Sciences**  
**University of Virginia**  
**Charlottesville, Virginia 22903**

**Introduction**

The mountains of western Virginia and the Shenandoah National Park (SNP) include lands of exceptional ecological significance. However, natural, industrial, agricultural, and vehicular atmospheric emissions of sulfur and nitrogen both inside and outside the region threaten the ecological integrity of many natural resources in the area. Sensitive aquatic and terrestrial resources, particularly those at higher elevations, can be degraded by existing or future pollution. Although increased atmospheric ozone and decreased visibility result from this pollution, the most serious threat to aquatic and terrestrial resources in the region arise from the acidifying effects of the sulfur and nitrogen deposition. The potential for ecosystem damage arising from acidic deposition was recognized in the 1990 Clean Air Act Amendments (CAAA) and Title IV of that act mandated a nationwide reduction in emissions of sulfur and nitrogen oxides from electric generators, a major contributor to acidic deposition. Now, nearly ten years after the enactment of the CAAA, significant reductions in emissions are being achieved. Several questions naturally arise. Have historical emissions (those emissions in the decades prior to the enactment of the CAAA) affected aquatic resources in the region? Have the mandated emissions reductions had an effect in the Shenandoah National Park? If so, how large? Are systems recovering or is acidification merely slowing down? If not, why not? Are larger reductions needed in the region? The answers to these management-related questions require the

development of tools (models) that can be used to assess current, past and future responses of aquatic resources to atmospheric deposition. Important products of this SNP:FISH project are models that incorporate the knowledge gained in the project about acidification effects on fish in the SNP.

For the past twenty years, we have been studying the effects of acidic deposition in the mountains of Virginia. Our research has focused on processes at various spatial scales from plot to hillslope to catchment to landscape, and has covered the temporal scale from individual storm processes (hours) to long-term monitoring (decades). This broad coverage has arisen from many individual projects, each focused on one or several particular aspects of the acidification problem. Some projects have ended, others have developed into long-term monitoring and data collecting. Over the years we have thus obtained many related data sets on a wide range of effects of acidic deposition in the mountains of Virginia. Now, as a result of this SNP:FISH project, we can relate the responses of fish at the individual, population, and community level to acidification of streams in the region, that is we can now link water-quality changes to potential fish damage. These data sets and linkages are a unique resource with which we can construct models that have both scientific and management utility; models that can aid our understanding of the complex interactions in the stream ecosystems and can quantify expected responses.

In the course of our research (and deriving directly from it), we developed a simulation model of the acidification process. The Model of Acidification of Groundwater In Catchments (MAGIC) was the principal model used by the National Acid Precipitation Assessment Program (NAPAP) scientists in the 1991 assessment of potential future damage to lakes and streams in the eastern United States. MAGIC is still being used in the U.S. (by EPA, the National Park Service, and the Forest Service) for policy-related assessments and has also been extensively used in Europe for assessment and policy formulation.

The data sets described above can be used with MAGIC to provide one of the most thoroughly calibrated regional applications of the model yet completed. This regionally calibrated model would be the ideal tool for prospective and retrospective analyses of resource responses to changed deposition in western Virginia. As part of this SNP:FISH project, we have incorporated the linkages between water quality and fish responses for SNP streams. Chapter 7 of this report describes in detail the model, its structure, and the incorporated fish responses. Chapter 7 also gives details of the calibration of the model for the three Intensively studied

SNP:FISH streams (Paine Run, Piney Run and Staunton River). This chapter is intended to give an overview of the model, a summary of its conceptual basis, a description of the data and procedures used to calibrate it, and an explanation of its potential uses as a management tool in the SNP.

## **End Users**

The new revisions to MAGIC provided as a result of the SNP:FISH project will be of immediate interest to both the scientific community and to environmental managers and decision makers. The National Park Service and the National Forest Service manage extensive lands in the region and have expressed interest in these types of integrated analyses. Several agencies of the Commonwealth of Virginia also manage land and other resources in the area and are likewise interested. Public interest groups such as Trout Unlimited, the Sierra Club and the Nature Conservancy should find the results useful in their various public information activities. The aquatic and terrestrial ecosystems in the mountains of Virginia are typical in many respects of the entire range of the southern Appalachian mountains. We anticipate that the results from this project will be of use to the same federal agencies and similar state and private concerns from Maryland to Georgia.

## **Application of the MAGIC Model to Sites in Shenandoah National Park**

The MAGIC model of stream and catchment responses to atmospheric deposition (version 5.01) was modified to include the fish effects established in this project. The modified version of the model was named MAGIC:FISH (version 5.01). The model was then applied to each of the intensively studied sites for which bioassays were performed (Paine Run, Piney Run and Staunton River). The details of the incorporation of the fish responses into MAGIC and the calibration results for the three catchments are described in Chapter 7.

The material in this chapter is intended to provide an overview of the protocol for applying MAGIC:FISH that might be used by SNP management personnel in response to future assessment needs. Copies of the model that can be run on PC computers and the calibrated parameter files for each intensively studied stream are provided on the diskette accompanying this report.

This chapter provides:

- 1) a description of the MAGIC model and its prior uses in acid deposition studies;
- 2) a conceptual discussion of the dynamics of acidification as modelled by MAGIC;
- 3) a discussion of the approach taken and the data needed to calibrate the model;
- 4) details of the modeling protocol we used for applying MAGIC in the SNP:FISH project, including our procedures for data assembly and management, and a description of the output products;
- 5) suggested procedures for providing performance analysis of model calibrations;
- 6) suggested procedures for providing uncertainty estimates of simulated responses to scenario and strategy runs;
- 7) a generalized classification system for linking water quality changes to fish responses abstracted from this project for general use when details of episodic water quality and/or aluminum concentrations in streams are not available.

#### *1) Description of the MAGIC model*

The MAGIC model (Model of Acidification of Groundwater In Catchments; Cosby et al. 1985a-c) was the principal model used by the National Acid Precipitation Assessment Program (NAPAP) to estimate future damage to lakes and streams in the eastern United States (NAPAP 1991, Thornton et al. 1990). The validity of the model has been confirmed by comparison with estimates of lake acidification inferred from paleolimnological reconstructions of historical lake changes in pH (Sullivan et al. 1991, 1996) and with the results of several catchment-scale experimental acidification and de-acidification experiments (e.g., Cosby et al. 1995, 1996). MAGIC has been used to reconstruct the history of acidification and to simulate the future trends on a regional basis and in a large number of individual catchments in both North America and Europe (e.g., Lepistö et al. 1988; Whitehead et al. 1988; Cosby et al. 1989, 1990, 1994, 1996; Hornberger et al. 1989; Jenkins et al. 1990a-c; Wright et al. 1990, 1994; Norton et al. 1992). MAGIC was one of the models used in SAMI Phase I (Cosby and Sullivan, 1998).

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry. The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: 1) a section in which the

concentrations of major ions are assumed to be governed by simultaneous reactions involving sulfate adsorption, cation exchange, dissolution-precipitation-speciation of aluminum, dissolution-speciation of inorganic carbon and dissociation of organic acids; and 2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass and losses to runoff. As implemented in this project, the model is a two-compartment representation of a catchment. Atmospheric deposition enters the soil compartment and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream compartment, and the appropriate equilibrium equations are reapplied to calculate streamwater chemistry. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Model output for 15 stream water variables is typically considered in simulation exercises. These variables consist of the concentrations of 10 ions (H; Ca; Mg; Na; K; NH<sub>4</sub>; SO<sub>4</sub>; NO<sub>3</sub>; Cl; and total inorganic Al), the stream discharge (Q), the stream pH, the sum of base cation concentrations ( $SBC = Ca + Mg + Na + K + NH_4$ ), the sum of acid anion concentrations ( $SAA = Cl + SO_4 + NO_3$ ) and the charge balance alkalinity ( $CALK = SBC - SAA$ ). These variables are expressed in units of m/yr (or m/mo) for Q,  $\mu\text{mol/L}$  for inorganic Al, and  $\text{ueq/L}$  for all other variables. In addition, model output for 7 soil and soilwater variables are usually considered: the total base saturation and individual cation saturations for Ca, Mg, Na, and K, the soilwater pH and the Ca/Al ratio in soil water.

## *2) Conceptual discussion of the dynamics of acidification as modelled by MAGIC*

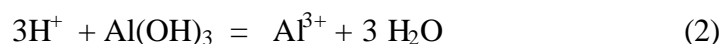
The most important effects of acidic deposition on catchment surface water quality are thought to be decreased pH and acid neutralizing capacity (ANC) and increased base cation and aluminum concentrations. In two papers, Reuss (1980, 1983) proposed a simple system of reactions describing the equilibrium between dissolved and adsorbed ions in the soil-soil water system. Reuss and Johnson (1985) expanded this system of equations to include the effects of carbonic acid resulting from elevated CO<sub>2</sub> partial pressure in soils, and demonstrated that large

changes in surface water chemistry should be expected as either CO<sub>2</sub> or sulfate concentrations varied in the soil water. The conceptual approach of Reuss and Johnson is attractive in that a wide range of observed catchment responses can be theoretically produced by a rather simple system of soil reactions.

Acid neutralizing capacity is generated in the soil water by the formation of bicarbonate from dissolved CO<sub>2</sub> and water:



The free hydrogen ion produced by this mechanism reacts with an aluminum mineral (e.g. gibbsite) in the soil:



Generally, the cation exchange sites on the soil matrix have a higher affinity for the trivalent aluminum cation than for di- or monovalent base cations. An exchange of cations between dissolved and adsorbed phases results:



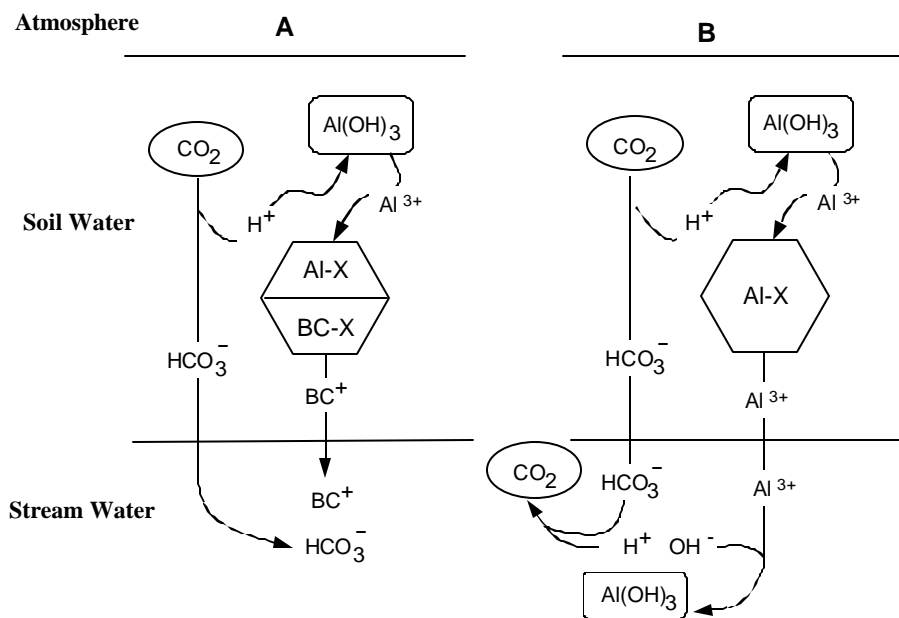
where BC<sup>+</sup> represents a base cation and X represents the soil exchange complex. The net result of these reactions is the production of ANC as bicarbonates of the base cations (e.g. Ca(HCO<sub>3</sub>)<sub>2</sub>).

As CO<sub>2</sub> partial pressure in the soil increases, the equilibrium reactions above proceed farther to the right hand side in each case, resulting in higher ANC in soil solution. If the soil water is removed from contact with the soil matrix and is exposed to the atmosphere (i.e. soil water enters the stream channel), the solution will degas CO<sub>2</sub> due to the lower atmospheric partial pressure of CO<sub>2</sub>. However, because the solution is no longer in contact with the soil, cation exchange reactions cannot occur. Changing the CO<sub>2</sub> partial pressure of a bicarbonate buffer solution will result in a change of pH but no net change in ANC. Thus, the ANC of the soil solution is equal to the ANC of the stream water, even though CO<sub>2</sub> partial pressure is generally much lower in surface waters.

These processes leading to the production of ANC in soil water and drainage water are illustrated in Figure 2-1A. The arrows indicate the net mass action effect on the equilibrium processes as the partial pressure of CO<sub>2</sub> in the soil increases. In this example a single base cation (BC<sup>+</sup>) is considered. In real systems all four base cations are present and have different affinities for the soil exchange sites. Dissolved trivalent aluminum (Al<sup>3+</sup>) can complex with dissolved



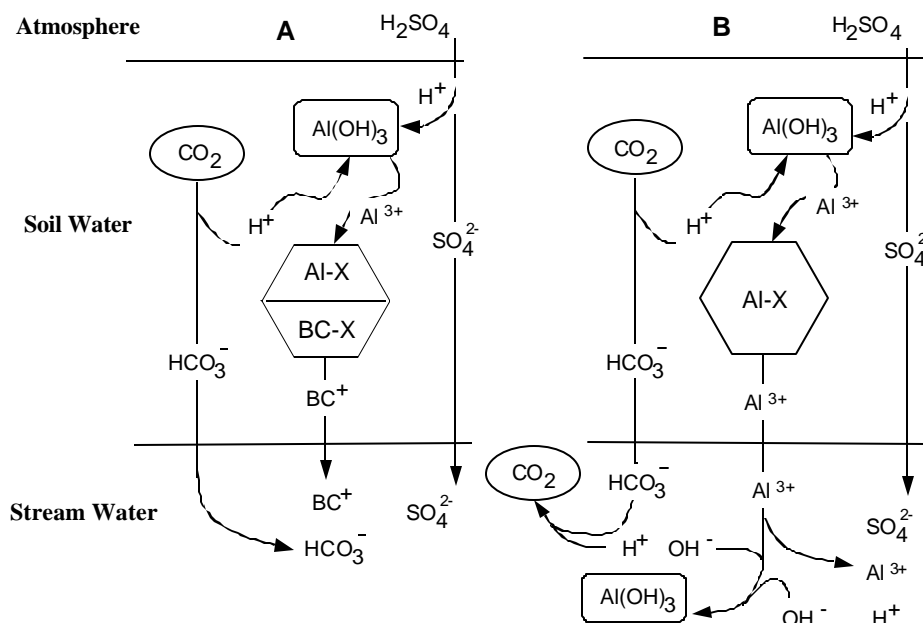
anions (e.g.,  $\text{SO}_4^{2-}$  or  $\text{F}^-$ ) or can be hydrated to form dissolved  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$ , and  $\text{Al}(\text{OH})_4^-$ . Organic acids can provide additional buffering of hydrogen ions. These complexities are ignored for the purposes of this conceptual discussion.



**Figure 2-1.** Schematic illustration of the responses of the system of soil reactions included in MAGIC in the absence of acidic deposition: A) with exchangeable base cations; and B) without exchangeable base cations.

If there are no exchangeable base cations on the soil matrix the situation is different (Figure 2-1B). Production of  $\text{HCO}_3^-$  and  $\text{H}^+$  from dissolved  $\text{CO}_2$  and dissolution of  $\text{Al}(\text{OH})_3$  proceed as before. However, there is no longer any possibility of exchange of  $\text{Al}^{3+}$  for base cations. The soil solution in this case consists of  $\text{HCO}_3^-$  and  $\text{Al}^{3+}$  ions. When the soil water enters the stream,  $\text{CO}_2$  degasses consuming one bicarbonate and one hydrogen ion for each molecule of  $\text{CO}_2$  lost. As the concentration of hydrogen ions decreases, the solubility of the aluminum solid phase is exceeded and Al precipitates as  $\text{Al}(\text{OH})_3$ , releasing  $\text{H}^+$  (the reverse of reaction 2). These reactions proceed until a new equilibrium is reached. If the same form of  $\text{Al}(\text{OH})_3$  precipitates in the stream as was dissolved in the soil, there is no net change in ANC.

Consider now what occurs when an external source of strong acid (atmospheric deposition) is added to the soil. Figure 2-2A shows the addition of  $\text{H}_2\text{SO}_4$  to a soil with exchangeable base cations. For the moment, we will assume that the  $\text{SO}_4^{2-}$  concentration is not affected as precipitation enters the soil (i.e., no sulfate adsorption). The hydrogen ions from atmospheric



**Figure 2-2.** Schematic illustration of the responses of the system of soil reactions included in MAGIC to the addition of  $\text{H}_2\text{SO}_4$  to a soil: a) with exchangeable base cations; and b) without exchangeable base cations. Catchments in sensitive settings exhibit responses to acidic deposition between these two extremes.

deposition dissolve additional  $\text{Al}^{3+}$  (relative to the case with no acidic deposition, Figure 2-1A) which in turn forces the cation exchange reactions to proceed further. However, the cation exchanges are equilibrium reactions. As the base cation concentrations increase, relatively less of the  $\text{Al}^{3+}$  will be exchanged. The amount of additional  $\text{Al}^{3+}$  that can be exchanged depends on the amount of exchangeable base cations on the soil. Soils with a large amount of exchangeable base cations will respond to acidic deposition by neutralizing essentially all of the atmospherically deposited  $\text{H}^+$ . Soils with a small amount of exchangeable base cations will be able to neutralize little of the atmospherically derived acidity. In either case, the initial effects of atmospheric deposition on catchment soils are increases in base cation concentrations, an

increase in  $\text{Al}^{3+}$  concentration, and (perhaps) a partial reduction of ANC in soil water. As the soil solution enters the stream, there is again no change in the net ANC of the soil solution. The base cation salts of bicarbonate and sulfate remain totally dissociated as the pH rises. The initial effect of adding a strong acid to the system is to increase the ionic strength of the streamwater. Stream ANC may or may not be reduced significantly. The magnitude of ANC decrease depends largely on the amount of exchangeable base cations on the soil.

If the  $\text{H}_2\text{SO}_4$  is added to the soil with no exchangeable base cations (Figure 2-2B), the acidity of the precipitation is not buffered. As before, the  $\text{SO}_4^{2-}$  passes through the system. The hydrogen ion deposited from the atmosphere dissolves  $\text{Al}^{3+}$ . No cation exchange occurs so all of the dissolved  $\text{Al}^{3+}$  enters the stream. When the solution degasses, that portion of the  $\text{Al}^{3+}$  produced by the carbonic acid is consumed as  $\text{Al}(\text{OH})_3$  precipitates. The excess  $\text{Al}^{3+}$  produced by the atmospheric hydrogen ion is not balanced by an equivalent amount of alkalinity. As the stream pH rises, some of the excess  $\text{Al}^{3+}$  ions precipitate, producing free  $\text{H}^+$  ions. The net result is acidic streamwater with a lower pH and a higher  $\text{Al}^{3+}$  concentration than in the undisturbed case.

The discussion so far has been concerned only with the initial mass action shifts in the equilibrium processes. These equilibria are assumed to occur instantaneously. The question arises: what controls the long term response of the catchment streamwater chemistry? Clearly, in the undisturbed case (Figure 2-1) the situation in a catchment would be expected to shift from that in Figure 2-1A to that in Figure 2-1B if there were no long term supply of base cations to replace those lost from the exchange sites. That long term supply must be the weathering of primary minerals in the catchment soils. If the system had been operating long enough to achieve a steady state, the output flux of base cations in the stream would equal the primary weathering input flux. For catchments with a primary mineral source of base cations, the steady state condition will resemble Figure 2-1A. The degree of base saturation (fraction of soil cation exchange sites occupied by base cations) at a steady state would be a function of the weathering rate, the cation selectivity of the soil and the hydrological response of the catchment.

If the steady state catchment is suddenly subjected to acidic deposition (Figure 2-2A), the excess base cations produced by the mobile anion effect must be derived from the exchangeable base cations of the soil. This assumes that primary mineral weathering is not increased by the acidic deposition. (This assumption seems valid since the net effect of the soil processes is to

buffer the soil pH. Changes in soil pH will lag the onset of acidic deposition. Unless soil solution pH changes, primary weathering will not be affected). The increased loss of base cations from the catchment will move the system away from the steady state. The base saturation of soils will decline and the system will move from the situation depicted in Figure 2-2A towards that shown in Figure 2-2B. If the acidic deposition remains constant at a high enough level, the stream base cation concentrations may eventually begin to decline after the initial increase due to the salt effect. When a new steady state is reached, the stream base cation concentrations will have returned to close to their pre-acidification levels (stream output of base cations equals unchanged weathering input of base cations). The increased mobile anion charge will be balanced by  $H^+$  and  $Al^{3+}$  and the stream alkalinity and pH will have declined. If deposition acidity exceeds the alkalinity of the catchment, the stream becomes acidic. The crucial questions are: How long will it take to reach the new steady state? What happens to the system during the transition? It is to address questions such as these that mathematical models of soil processes are developed.

### *3) Calibration approach and data needed for implementation of MAGIC*

The aggregated nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model that can be directly measured or observed in the system of interest (called fixed parameters). The model is then run (using observed and/or assumed atmospheric and hydrologic inputs) and the outputs (streamwater and soil chemical variables - called criterion variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called optimized parameters) are adjusted to improve the fit. After a number of iterations, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated. If new assumptions (or values) for any of the fixed variables or inputs to the model are subsequently adopted, the model must be re-calibrated by re-adjusting the optimized parameters until the simulated-minus-observed values of the criterion variables again fall within the specified tolerance.

The calibration procedure requires that stream water quality, soil chemical and physical characteristics, and atmospheric deposition data be available for each stream. The water quality data needed for calibration are the concentrations of the individual base cations (Ca, Mg, Na, and K) and acid anions (Cl, SO<sub>4</sub>, and NO<sub>3</sub>) and the stream pH. The soil data used in the model include soil depth and bulk density, soil pH, soil cation-exchange capacity, and exchangeable bases on the soil (Ca, Mg, Na, and K). The atmospheric deposition inputs to the model must be estimates of total deposition, not just wet deposition.

Soil physical and chemical properties - Soils data for model calibration are usually assigned to individual stream sites using a procedure that relies on areally averaged values of soil parameters sampled within the catchment. If no soils data are available within the catchment, observed data from sites on similar bedrock geology or within a similar landscape unit geographically closest to the stream site are used. If soils data for a given location are stratified by soil horizon, the soils data for the individual soil horizons at that sampling site are usually vertically aggregated (weighted by horizon depth and bulk density) to obtain single values for the site.

Atmospheric Deposition - Total atmospheric deposition consists of three components: wet deposition, the flux of ions occurring in precipitation; dry deposition, resulting from gaseous and particulate fluxes; and cloud/fog deposition which can be particularly important in mountainous areas. In addition to wet deposition data measured directly at sites within SNP, estimates of precipitation volume and of wet deposition of ions can be derived from the deposition model of Grimm and Lynch (1997). Their model provides spatially continuous estimates of precipitation volume and of sulfate, nitrate, chloride, hydrogen ion, calcium, ammonium, magnesium, potassium, and sodium concentration in precipitation using interpolated data from a national network of precipitation monitoring stations (the NADP sites) and weighted least-squares regression techniques to account for the influence of topography and elevation. Observations of dry deposition or cloud/fog deposition are very infrequent. Where those estimates are available (as in the Mountain Cloud Chemistry Project in SNP), the observed deposition rates can be combined with observed wet deposition to calculate the ratio of estimated total deposition to the observed wet deposition for important ions (e.g., sulfate, nitrate and ammonium ions). These

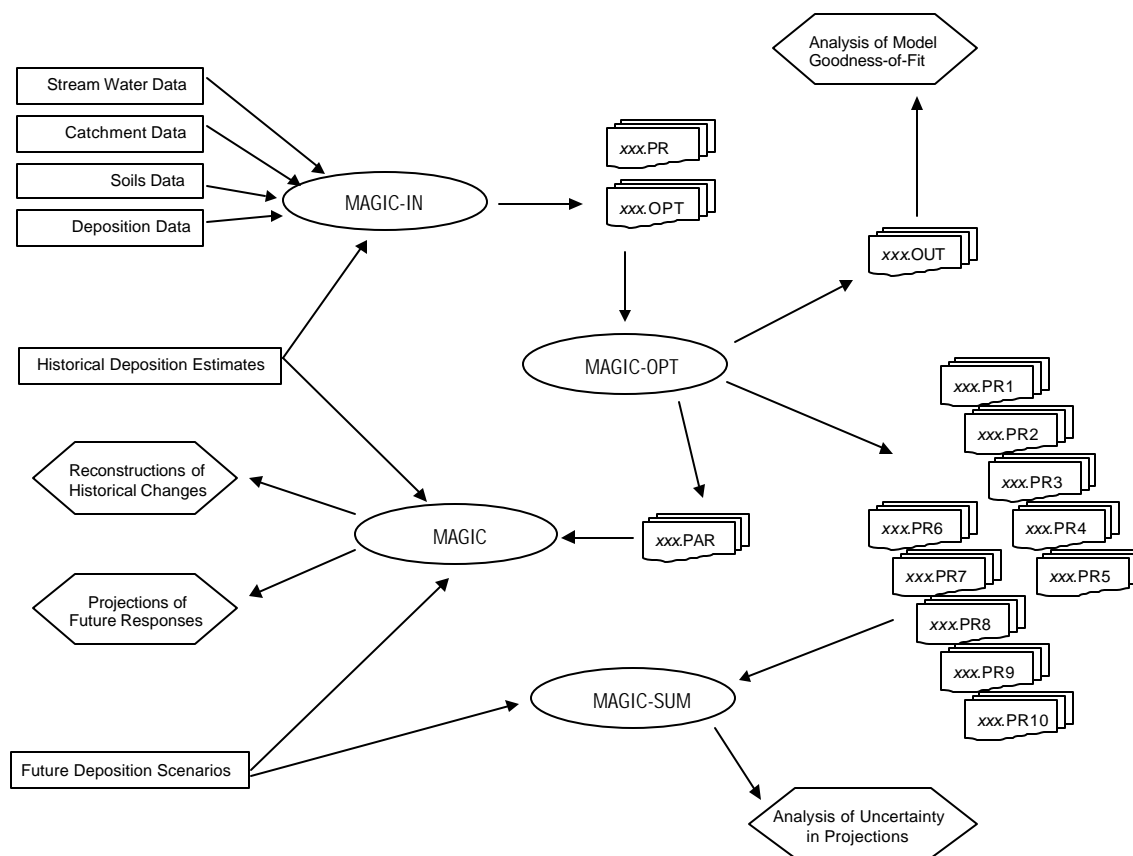
ratios (called dry deposition factors) can then be used to calculate total deposition from the estimated wet deposition data at sites for which dry deposition data are not available

Historical Loading - Calibration of the model (and estimation of the historical changes at the sites) requires a temporal sequence of historical anthropogenic deposition. Our current understanding of ecosystem responses to acidic deposition suggests that future ecosystem responses can be strongly conditioned by historical acidic loadings. Thus, we maintain that, as part of the model calibration process, the model should be constrained by some measure of historical deposition to the site. However, such long-term, continuous historical deposition data do not exist. We usually use historical emissions data as a surrogate for deposition. The emissions for each year in the historical period can be normalized to emissions in a reference year (a year for which observed deposition data are available). Using this scaled sequence of emissions, historical deposition can be estimated by multiplying the total deposition estimated for each site in reference year by the emissions scale factor for any year in the past to obtain deposition for that year. Emissions data for both SO<sub>2</sub> and NO<sub>x</sub> are available on a state-by-state basis back to the turn of the century.

#### *4) Protocol for MAGIC calibration and simulation at individual sites*

The protocol for applying MAGIC to an individual site involves a number of steps, uses a number of programs and produces several discrete outputs. Please refer to Figure 2-3 for the general discussion of the protocol in this section and when specific databases, files, or programs are mentioned in the following text.

The input data required by the model (stream water, catchment, soils, and deposition data) are assembled and maintained in data bases (electronic spreadsheets). When complete, these data bases are accessed by a program (MAGIC-IN) that generates the initial parameter files (xxx.PR) and optimization (xxx.OPT) files for each site within the landscape unit. The initial parameter files contain observed (or estimated) soils, deposition and catchment data for each site. The optimization files contain the observed soil and stream water data that are the targets for the calibration at each site, and the ranges of uncertainty in each of the observed values. The initial parameter and optimization files for each site are sequentially passed to the optimization program (MAGIC-OPT). This program produces three outputs as each site is calibrated. The first



**Figure 2-3.** Flow Diagram for MAGIC calibration and simulation. Rectangles represent databases required as inputs. The input databases are usually maintained in the form of electronic spreadsheets, with each spreadsheet having entries for each watershed in the analysis. Ovals represent the suite of MAGIC programs used in the calibration and simulation procedures. All programs are compiled for execution on personal computers using MS-WINDOWS operating systems. Communication among the programs is accomplished using ASCII coded files (multiple-page icons in the figure) which can be viewed using text editors. One of each type of file (as indicated by the extension following the period) is produced and archived for each catchment (as indicated by the xxx preceding the period). Hexagons represent the results and outputs of the procedure. The results are usually maintained in the form of electronic spreadsheets, with each spreadsheet having entries for each watershed in the analysis. The results of the reconstructions and future projections for individual catchments will be used as inputs for analyses of biological responses and for extrapolation of regional responses. The input databases, programs, and results data bases are described individually in the text.

(xxx.OUT) is an ASCII file of results that will be passed to statistical routines for analysis and summary of model goodness-of-fit for the site. The second (xxx.PR1 ... xxx.PR10) are the multiple calibrated parameter sets used in the fuzzy calibration procedure to assess model uncertainty. The third (xxx.PAR) is the average parameter set for each site (average of the fuzzy calibration parameter sets). This parameter set represents the most likely responses of the site and will be used for scenario and strategy analyses.

The average calibrated parameter set (xxx.PAR) for each site is used by MAGIC with estimates of historical or future deposition to produce two outputs: 1) reconstructions of historical change at the site; or 2) forecasts of most likely future responses for the applied future deposition scenario. Both of these outputs can be stored in the form of electronic spreadsheets giving simulated values for all modeled variables for each year of each scenario at the site. In a like manner, the multiple fuzzy parameter sites are used with the same estimates of future deposition and the summary program (MAGIC-SUM) to produce an analysis of the uncertainty in model projections for that scenario. The results of the uncertainty analysis can be in the form of an electronic spreadsheet giving simulated ranges (upper and lower values) for all modeled variables for each year of each scenario at the site.

The implementation of this protocol provides a structure for quality control and serves to document the calibration procedure, providing a degree of objectivity in the calibration process. The assumptions involved in the calibration of MAGIC for a given site become "set" (and are implicitly documented in the electronic spreadsheets and output files) once a final calibration protocol is adopted. That is, anyone given the input files and programs in Figure 2-3 will generate the same intermediate and final products for each site. There are no subjective decisions made during the calibration of any site that may be forgotten, obscured or confused. This, in turn, helps to keep any subjective bias in calibration from affecting scenario or strategy simulations. A similar objective protocol was used for MAGIC applications in NAPAP and has been used by us in a number of regional studies in the US and Europe. The objective and sequential structure of this protocol also provides a convenient framework for assessing the status of the modeling effort at any time in a project (where are we in the flow diagram, how many more sites remain, etc.).



#### *5) Performance analysis for calibrations*

When the model is calibrated to a site, some measures of model goodness-of-fit (performance measures) are needed to assess the validity and success of the calibration before simulations are run. We routinely generate and compare summary statistics (mean, standard deviation, maximum and minimum) for the observed values, the simulated values and the differences (simulated-observed values) of each of the 15 stream variables and each of the 7 soil variables for each site to which the model is applied. In addition, plots of simulated versus observed values for stream and soil variables can be constructed and examined if time series of data are available. These analyses will allow determination of whether or not the model calibration results are biased or contain residual errors that may be too large.

#### *6) Uncertainty estimates for simulated responses to scenario runs;*

The estimates of the fixed parameters, deposition inputs and the target variable values to which the model is calibrated are all subject to uncertainties (errors in the observed or estimated values used as inputs). A multiple-optimization procedure can be implemented for calibrating the model that will allow estimation of the effects of these uncertainties on simulated values once the model is calibrated. This optimization procedure consists of multiple calibrations of each site using random values of the fixed parameters drawn from the observed range of values, and random values of deposition from the range of model estimates. Each of the multiple calibrations begin with (1) a random selection of values of fixed parameters and deposition, and (2) a random selection of the starting values of the adjustable parameters. The adjustable parameters are then optimized to achieve a minimum error fit to the target variables. This procedure is repeated ten times for each site. The final calibrated model is represented by the ensemble of parameter values and variable values of the successful calibrations. To provide an estimate of the uncertainty (or reliability) of a simulated response to a given scenario, all of the ensemble parameter sets are run using the scenario. For any year in the scenario, the largest and smallest values of simulated variable define the upper and lower confidence bounds for that site's response for the scenario under consideration. Applied for all variables and all years of the scenario (program MAGIC-RUN in Figure 2-3), this procedure results in a band of simulated values through time that encompasses the likely response of the site for any point in the scenario.

The distributions of these uncertainty estimates for each landscape unit can be regionalized to provide overall estimates of uncertainty for a scenario applied to an entire region of interest.

#### 7) *Classification of biological status from water quality*

We have developed (from the results of this SNP:FISH project) a general classification system for biological responses of fish defined by the average annual (volume-weighted) mean value of stream acid neutralizing capacity (ANC). The scheme is intended for use when details of episodic water quality and/or aluminum concentrations in streams are not available and the more detailed fish response models described elsewhere in this report cannot be applied. The scheme is based on stream ANC to provide a linkage to the MAGIC model. The scheme relies on the fact that there are strong correlations among those water quality variables that determine fish responses. For instance, streams that have high annual average ANC are not subject to acid episodes (and the associated deleterious effects on fish). As annual average ANC declines, the frequency and intensity of acid episodes will increase. Thus, in the absence of episodic data, estimates of annual average ANC from routine stream monitoring still provides robust information about the likely fish status within a stream.

We have for SNP developed four-category classification scheme in which the ANC ranges of the four classes presented are chosen to represent thresholds for responses of brook trout to acidic conditions (Table 2-1 and below). Given the relatively broad ANC intervals used, the same classes can also be applied for other fish species in SNP.

**Table 2-1:** Generalized fish response categories and ANC classes.

<b>Response</b>		<b>ANC Range</b>	
<b>Category</b>	<b>ANC Class</b>	<b>meq L<sup>-1</sup></b>	<b>Brook Trout Response</b>
Suitable	Not acidic	> 50	Reproducing brook trout populations expected where habitat suitable
Indeterminate	Indeterminate	20-50	Extremely sensitive to acidification; brook trout response variable
Marginal	Episodically acidic	0-20	Sub-lethal and/or lethal effects on brook trout possible
Unsuitable	Chronically acidic	< 0	Lethal effects on brook trout probable

Streams that are *not acidic* (annual average ANC greater than 50  $\mu\text{eq L}^{-1}$ ) are generally *suitable* for brook trout because they have a large enough buffering capacity that persistent acidification poses no threat to brook trout and there is little likelihood of storm-induced acid episodes lethal to brook trout. The ANC in these streams typically remains above zero in all seasons and flow regimes. As a result, reproducing brook trout populations are expected. ANC values below 200  $\mu\text{eq L}^{-1}$  have been regarded elsewhere as "sensitive" to acidification for general ecological purposes (Altshuller and Lindhurst 1984; Winger et al. 1987; Knapp et al. 1988). Bulger et al. (1995), examining brook trout response only, set the threshold for unaffected streams much lower because brook trout are a relatively acid tolerant species.

Streams that we term *indeterminate* (annual average ANC from 20 to 50  $\mu\text{eq L}^{-1}$ ) comprise a problematic category for prediction of both acid deposition effects and brook trout status. Streams in this category have been designated elsewhere as "extremely sensitive" to acidification (Gibson et al. 1983; Schindler 1988), because any further reduction in ANC can produce extremely deleterious biological effects. In this range of average annual ANC, streams may or may not experience lethal episodic acidification during storms. The occurrence of episodic acidity depends on a number of hydrologic, physical, and chemical characteristics that cannot be readily predicted, such as the ratio of stormflow to baseflow (a function of the geomorphology of the catchment and storm severity), and the occurrence of springs or minor alkaline tributaries (that can buffer storm events at these levels of ANC). The status of brook trout populations is also difficult to predict in these streams. Brook trout populations can be healthy if other habitat characteristics are favorable or poor if the habitat quality declines. In general, membership in this category can be regarded as transient, as streams shift between the not acidic and episodically acidic categories (and brook trout status shifts between suitable and marginal) during acidification and recovery from acidification.

Streams that are *episodically acidic* (annual average ANC from 0 to 20  $\mu\text{eq L}^{-1}$ ) are *marginal* for brook trout because they have so little buffering capacity that acid episodes are likely (Hyer et al., 1995). Although the frequency and magnitude of episodes varies, streams in this category have already lost sensitive fish species, and display a reduced species richness. Examples of species lost might include longnose dace, mottled sculpin, northern hog sucker, central stoneroller, river chub, and rosyside dace (Heard et al., in press; Bulger et al., 1995; Bulger et al., 1995). There are measurable sub-lethal stresses on individuals in these streams,

including low body weight and condition factor in blacknose dace and brook trout (Dennis et al., 1995; Dennis and Bulger, 1995), and lower population density in brook trout, (Bulger et al., 1995) and other more acid-tolerant species (Bulger et al., 1995). Missing year classes of brook trout also become more likely. Streams in this category can have baseflow chemistry tolerable to brook trout fry but acidic episodes lethal to fry (MacAvoy and Bulger, 1995).

Streams that are *chronically acidic* (annual average ANC less than  $0 \mu\text{eq L}^{-1}$ ) are *unsuitable* for brook trout. Forested, headwater streams in the mountains of Virginia with annual average ANC's less than zero have negative ANC's for most of the year, not just during storm events. As a result, the biological communities of streams in this category are severely affected. Loss of even acid-tolerant species occurs in these streams, and species richness is very low. Such streams cannot support healthy brook trout populations.

### **MAGIC Calibrations for the Intensively Studied Sites - Model Deliverables**

MAGIC was calibrated for the three Intensively studied sites as described above. The results are presented and discussed in Chapter 7. The calibrated parameter files and an executable copy of the MAGIC:FISH model are included on the CD-ROM that accompanies this report. The model was calibrated as described in Figure 2-3. The input files for the calibration (xxx.pr and xxx.opt), the successful fuzzy calibration parameter sets (xxx.PRY) and the summary statistics and model goodness-of-fit for the calibrations (xxx.OUT) are saved on the CD-ROM in a separate sub-directory for each site (Paine Run, Piney River and Staunton River). The executable model code and the average parameter file for each site (xxx.PAR) are stored in the MAGIC-FISH directory on the CD-ROM.

## References

- Booty, W. G., and J. R. Kramer. 1984. Sensitivity analysis of a watershed acidification model. *Philos. Trans. R. Soc. London, Ser. B*, 305:441-449.
- Cosby, B.J. 1998. Modelling the Biological Effects of Water Quality Changes in the streams of the FISH Catchments. Chapter 7 in: Final Report of the FISH (Fish In Sensitive Habitats) Project - An Integrated Assessment of Fish Community Responses to Stream Acidification in Shenandoah National Park, VA. A.J. Bulger, ed. University of Virginia.
- Cosby, B.J., R.C. Ferrier, A. Jenkins, B.A. Emmett, R.F. Wright and A. Tietema. 1997. Modelling the ecosystem effects of nitrogen deposition at the catchment scale: model of ecosystem retention and loss of inorganic nitrogen (MERLIN). *Hydrology and Earth System Sciences* 1:137-158.
- Cosby, B.J., R.F. Wright, and E. Gjessing. 1995. An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway. *J. Hydrol.* 170:101-122.
- Cosby, B. J., G. M. Hornberger, R. F. Wright, and J. N. Galloway. 1986. Modeling the effects of acid deposition: Control of long-term sulfate dynamics by soil sulfate adsorption, *Water Resour. Res.* 22(8):1283-1302.
- Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway. 1985a. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.* 21:51-63.
- Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway. 1985b. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Water Resour. Res.* 21:1591-1601.
- Cosby, B.J., G.M. Hornberger, J.N. Galloway, and R.F. Wright. 1985c. Time scales of catchment acidification: a quantitative model for estimating freshwater acidification. *Environ. Sci. Technol.* 19:1144-1149.
- Cosby, B. J., R. F. Wright, G. M. Hornberger and J. N. Galloway. 1984a. Model of acidification of groundwater in catchments. Project completion report, Proj. E2-14, EPA/NCSU Acid Precipitation Program, Environ. Prot. Agency, N. C. State Univ., October 1984.
- Christophersen, N. and R.F. Wright. 1981. A model for streamwater chemistry at Birkenes, Norway. *Water Resour. Res.* 17:377-389.
- Christophersen, N., H.M. Seip, and R.F. Wright. 1982. A model for streamwater chemistry at Birkenes, Norway. *Water Resour. Res.* 18:977-997.

- Couto, W., D. J. Lathwell, and D. R. Bouldin. 1979. Sulfate sorption by two oxisols and an alfisol of the tropics, *Soil Sci.* 127:108-116.
- David, M.B. and G.F. Vance. 1991. Chemical character and origin of organic acids in streams and seepage lakes of central Maine. *Biogeochemistry* 12:17-41.
- Dise, N.B. and R.F. Wright. 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecol. Management* 71:153-163.
- Driscoll, C.T., M.D. Lehtinen, and T.J. Sullivan. 1994. Modeling the acid-base chemistry of organic solutes in Adirondack, New York, lakes. *Water Resour. Res.* 30:297-306.
- Emmett, B.A., D. Boxman, M. Bredemeier, F. Moldan, P. Gundersen, O.J. Kjonaas, P. Schleppi, A. Tietema and R.F. Wright. 1998. Predicting the effects of atmospheric nitrogen deposition in conifer stands: evidence from the NITREX ecosystem-scale experiments. *Ecosystems*.
- Emmett, B.A., B.J. Cosby, R.C. Ferrier, A. Jenkins, A. Tietema and R.F. Wright. 1997. Modelling the ecosystem effects of nitrogen deposition at the catchment scale: simulation of nitrogen saturation in a Sitka spruce forest, Aber, Wales, UK. *Biogeochemistry* 38:129-148.
- Emmett, B.A., P.A. Stevens and b. Reynolds. 1995. Factors influencing nitrogen saturation in Sitka spruce stands in Wales. *Water Air Soil Pollut.* 85:1629-1634.
- Emmett, B.A., B. Reynolds, P.A. Stevens, D.A. Norris, S. Hughes, J. Gorres and I. Lubrecht. 1993. Nitrate leaching from afforested Welsh catchments - interactions between stand age and nitrogen deposition. *Ambio* 22:386-394.
- Ferrier, R.C., A. Jenkins, B.J. Cosby, R.C. Helliwell, R.F. Wright, and A.J. Bulger. 1995. Effects of future N deposition scenarios on the Galloway region of Scotland using a coupled sulphur & nitrogen model (MAGIC-WAND). *Water Air Soil Pollut.* 85:707-712.
- Gaines, G. L., and H. C. Thomas. 1953. Adsorption studies on clay minerals, II. A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.* 21:714-718.
- Gjessing, E.T. 1994a. HUMEX (Humic Lake Acidification Experiment): chemistry, hydrology and meteorology. *Environ. Int.* 20:267-276.
- Gjessing, E.T. 1994b. The role of humic substances in the acidification response of soil and water - results of the Humic Lake Acidification Experiment (HUMEX) *Environ. Int.* 20:363-368.
- Goldstein, R. A., S. A. Gherini, C. W. Chen, L. Mak, and R. J. M. Hudson. 1984. Integrated acidification study (ILWAS): A mechanistic ecosystem analysis. *Phil. Trans. R. Soc. London., Ser. B*, 305:409-425.

- Gundersen, P., B.A. Emmett, O.J. Kjonaas, C.J. Koopmans and A. Tietema. 1998. Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. *Forest Ecol. Management* 101:37-55.
- Hasan, S. M., R. L. Fox, and C. C. Boyd. 1970. Solubility and availability of sorbed sulfate in Hawaiian soils. *Soil Sci. Soc. Am. Proc.* 34:897-901.
- Jenkins, A., R.C. Ferrier and B.J. Cosby. 1996. A dynamic model for assessing the impact of coupled sulphur and nitrogen deposition scenarios on surface water acidification. *J. Hydrol.* 197:111-127.
- Jenkins, A. and B.J. Cosby. 1989. Modelling surface water acidification using one and two soil layers and simple flow routing. In: J. Kamari, D.F. Brakke, A. Jenkins, S.A. Norton and R.F. Wright (eds), *Regional Acidification Models: Geographic Extent and Time Development*, Springer, New York, 1989, pp. 253-266.
- McKnight, D.M., E.M. Thurman, R.L. Wershaw and H.F. Hemond. 1985. Biogeochemistry of aquatic humic substances in Thoreau's Bog, Concord, Massachusetts. *Ecology* 66:1339-1352.
- Oliver, B.G., E.M. Thurman, and R.L. Malcolm. 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochim. Cosmochim. Acta* 47:2031-2035.
- Oreskes, N., K. Schrader-Frechette and K. Belitz. 1994. Verification, validation and confirmation of numerical models in the earth sciences. *Science* 263:641-646.
- Rastetter, E. B., A. W. King, B. J. Cosby, G. M. Hornberger, R. O. O'Neill, and J. E. Hobbie. 1992. Aggregating fine-scale ecological knowledge to model coarser-scale attributes of ecosystems, *Ecolog. Applic.* 2:55-70.
- Reuss, J. O. 1983. Implications of the Ca-Al exchange system for the effect of acid precipitation on soils. *J. Environ. Qual.* 12:591-595.
- Reuss, J. O. 1980. Simulations of soil nutrient losses resulting from rainfall acidity. *Ecol. Model.* 11:15-38.
- Reuss, J. O., and D. W. Johnson. 1985. Effect of soil processes on the acidification of water by acid deposition. *J. Environ. Qual.* 14:26-31.
- Schecher, W.D. and C.T. Driscoll. 1993. ALCHEMI: A chemical equilibrium model to assess the acid-base chemistry and speciation of aluminum in dilute solutions. In R. Loeppert, A.P. Schwab, and S. Goldberg. *Chemical Equilibrium and Reaction Models*. Soil Sci. Soc. Amer., Madison, WI.

- Schnoor, J. L., W. D. Palmer, Jr., and G. E. Glass. 1984. Modeling impacts of acid precipitation for northeastern Minnesota. In Schnoor, J.L. (ed.). Modeling of Total Acid Precipitation Impact. Butterworth, Boston, Mass. pp. 155-173.
- Stoddard, J.L. 1994. Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. In: L. Baker (ed) Environmental Chemistry of Lakes and Reservoirs. Advances in Chemistry Series, No. 237, American Chemical Society, Washington, D.C., pp 223-284.
- Sullivan, T.J. and B.J. Cosby. 1998. Modeling the Concentration of Aluminum in Surface Waters. Water Air Soil Pollut. 105:643-659.
- Sullivan, T.J., B.J. Cosby, C.T. Driscoll, D.F. Charles, and H.F. Hemond. 1996. Influence of organic acids on model projections of lake acidification. Water Air Soil Pollut. 91:271-282.
- Sullivan, T.J., B.J. Cosby, S.A. Norton, D.F. Charles, R.F. Wright and E. Gjessing. 1995. Multi-site testing and evaluation of a geochemical model of acid-base chemistry - confirmation of the MAGIC model using catchment manipulation experiments and historical diatom inferences. In: Ecosystem Manipulation Experiments: scientific approaches, experimental design and relevant results. A. Jenkins, R.C. Ferrier and C. Kirby (eds). Ecosystems Research Report 20, Commission of European Communities, Luxembourg, pp.360-365.
- Tietema, A. and C. Beier. 1995. A correlative evaluation of nitrogen cycling in the forest ecosystems of the EC projects NITREX and EXMAN. Forest Ecol. Management 71: 143-151.
- Wright, R.F. and N. van Breemen. 1995. The NITREX project: an introduction. Forest Ecol. Management 71:1-5.
- Wright, R.F., E. Lotse, and A. Semb. 1993. RAIN Project: Results after 8 years of experimentally reduced acid deposition to a whole catchment. Can. J. Fish. Aquat. Sci. 50:258-268.
- Wright, R.F. 1989. RAIN project: role of organic acids in moderating pH change following reduction in acid deposition. Water Air Soil Pollut. 46:251-259.



**SNP:FISH**  
**Shenandoah National Park: Fish In Sensitive Habitats**  
**Project Final Report, Volume I**

**Appendix**

**Maps of the SNP:FISH Catchments**

**Catchment Boundaries, Stream Networks, Sampling Sites**

**Distributions of Vegetation and Bedrock Geology**

**Prepared by**

**Rick Webb**

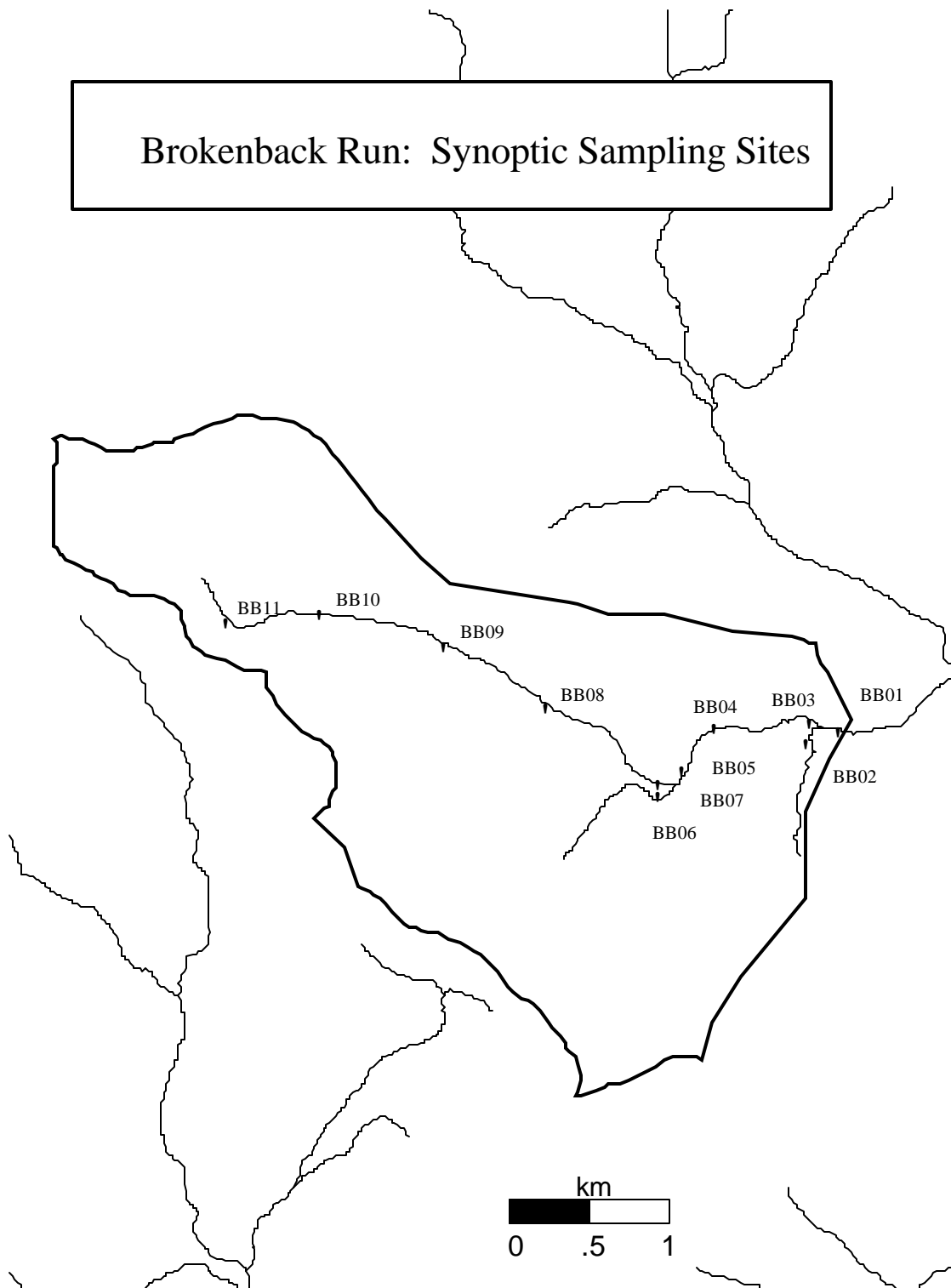
**Department of Environmental Sciences**

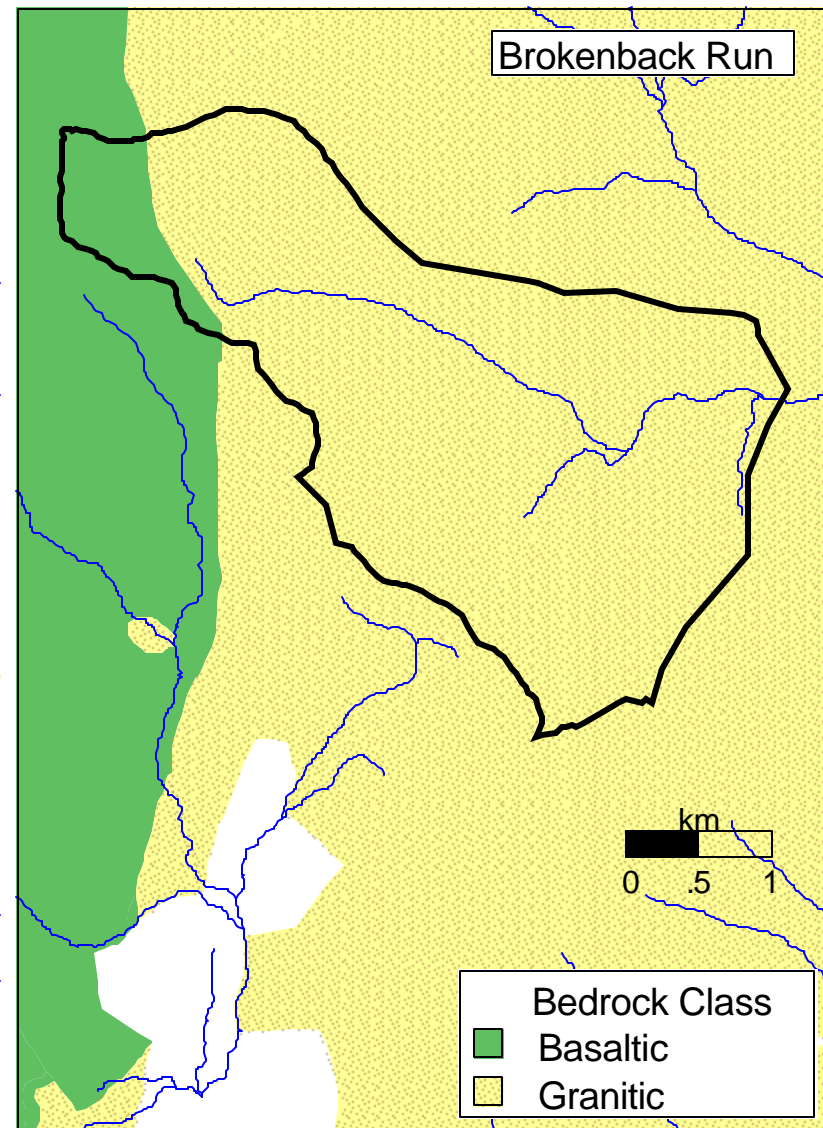
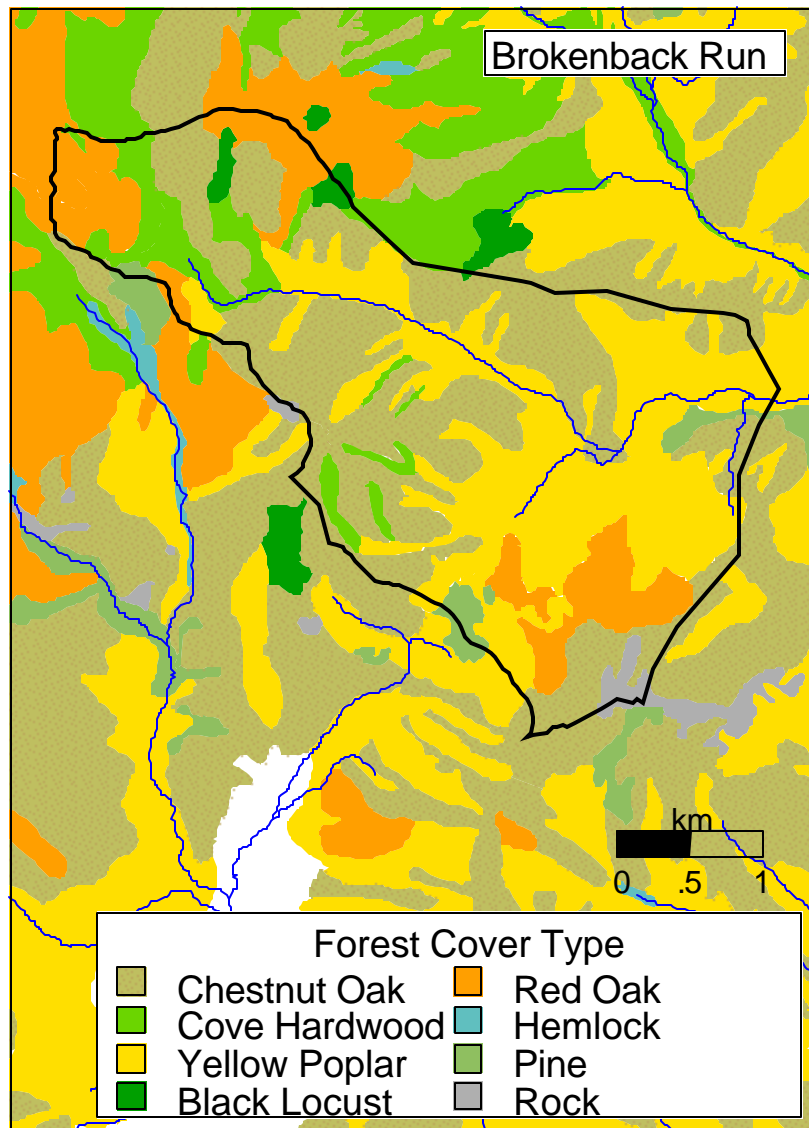
**University of Virginia**

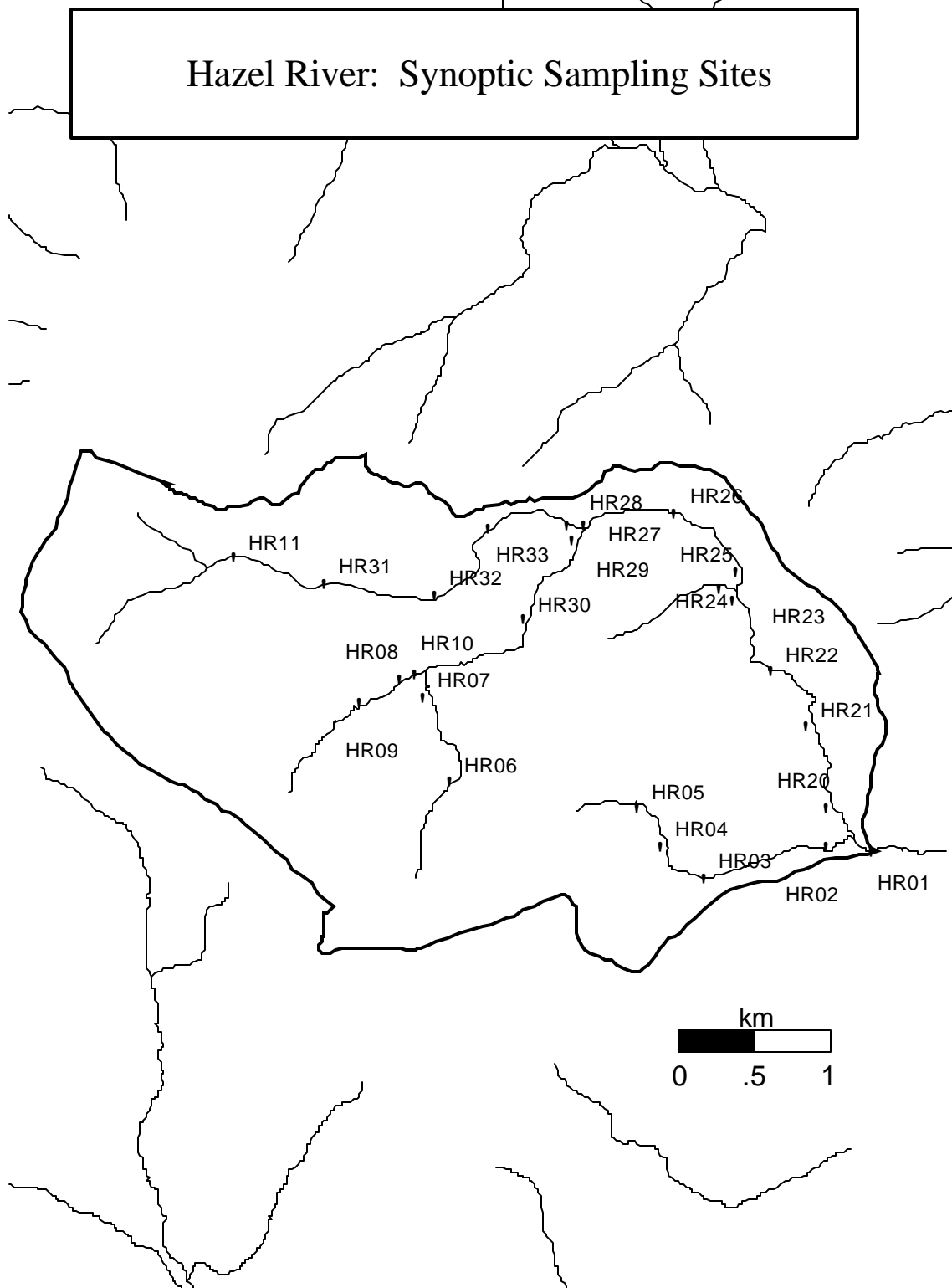
**Charlottesville, Virginia 22903**

The Locations within the Shenandoah National Park of the Catchments Included in the Appendix are given on the map below.

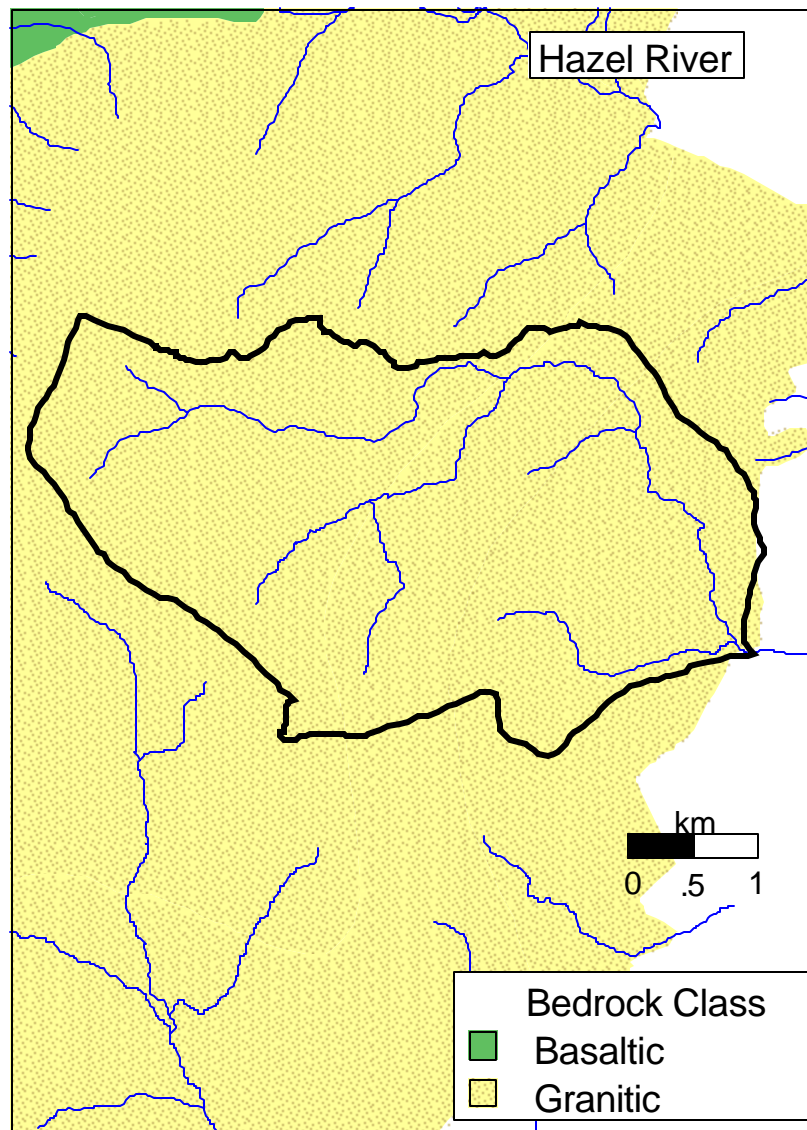
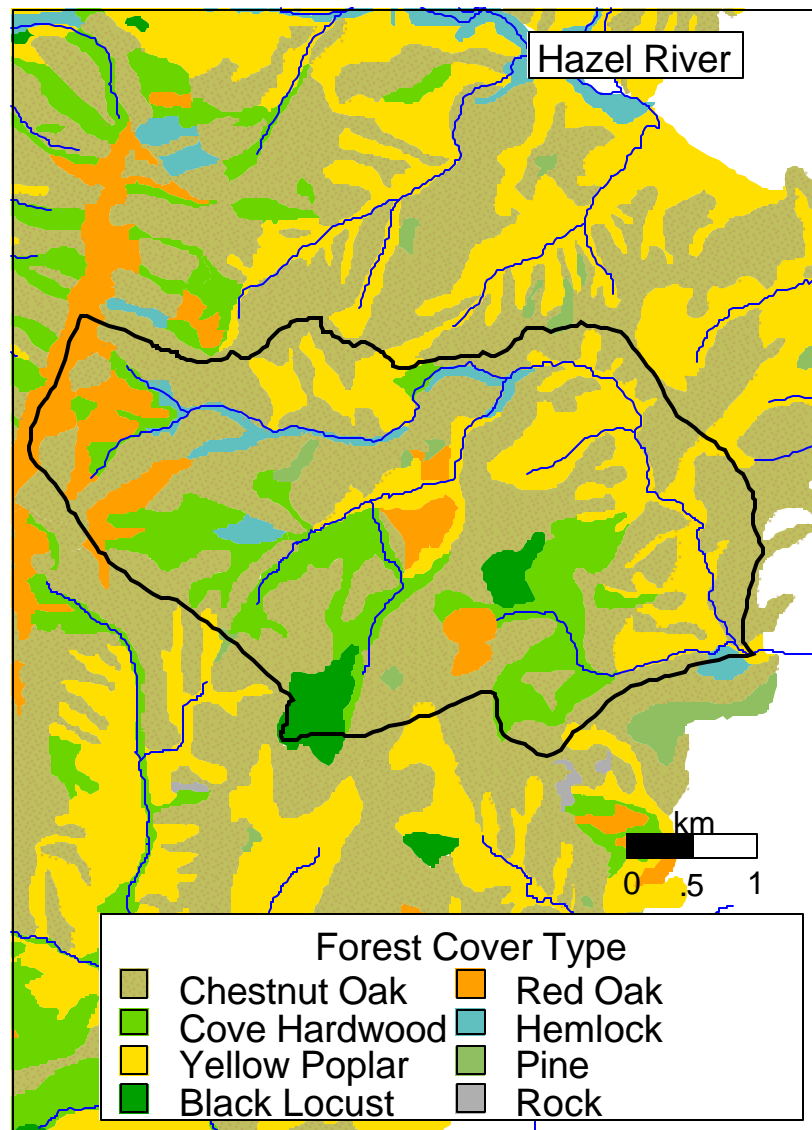


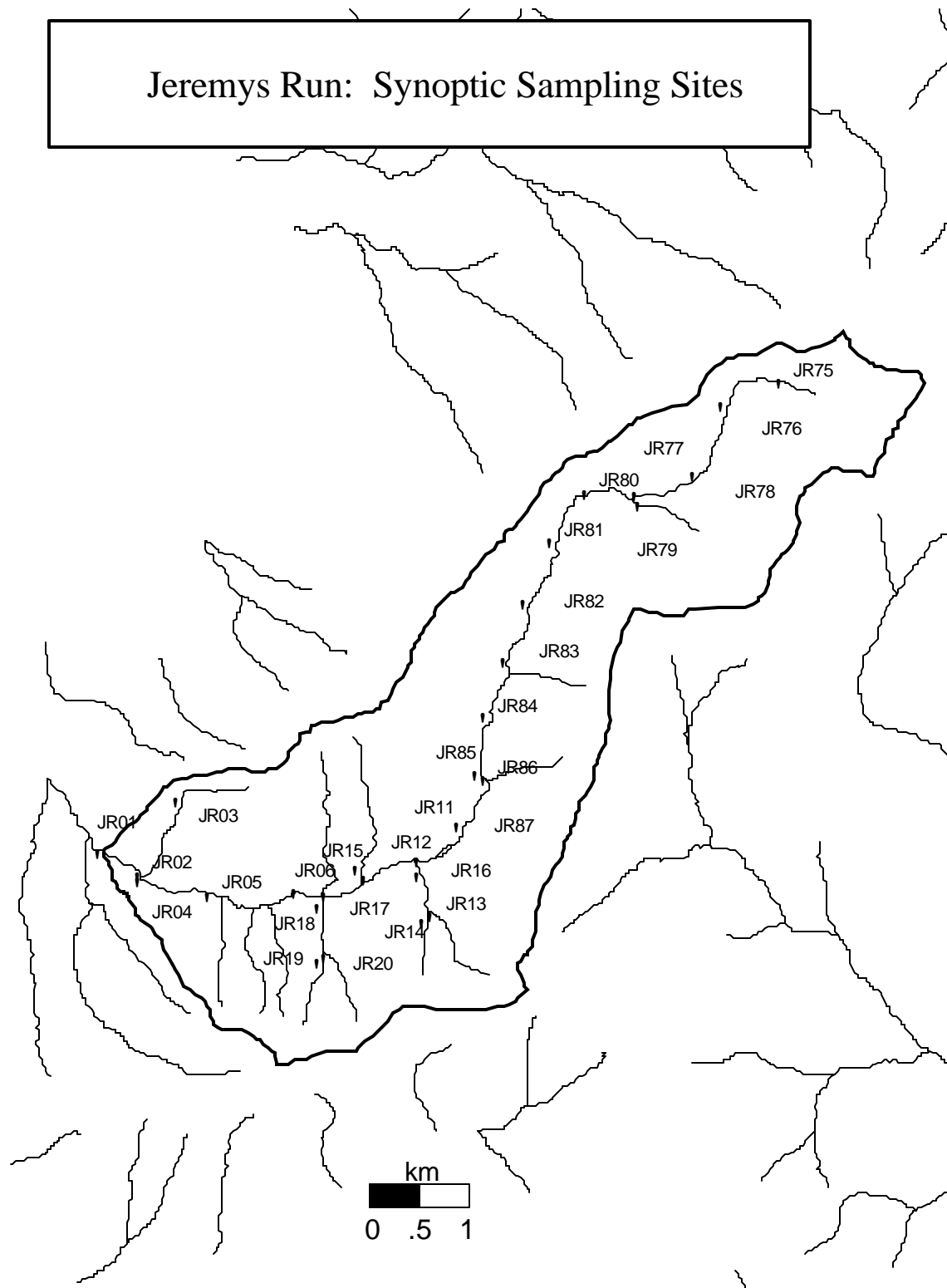




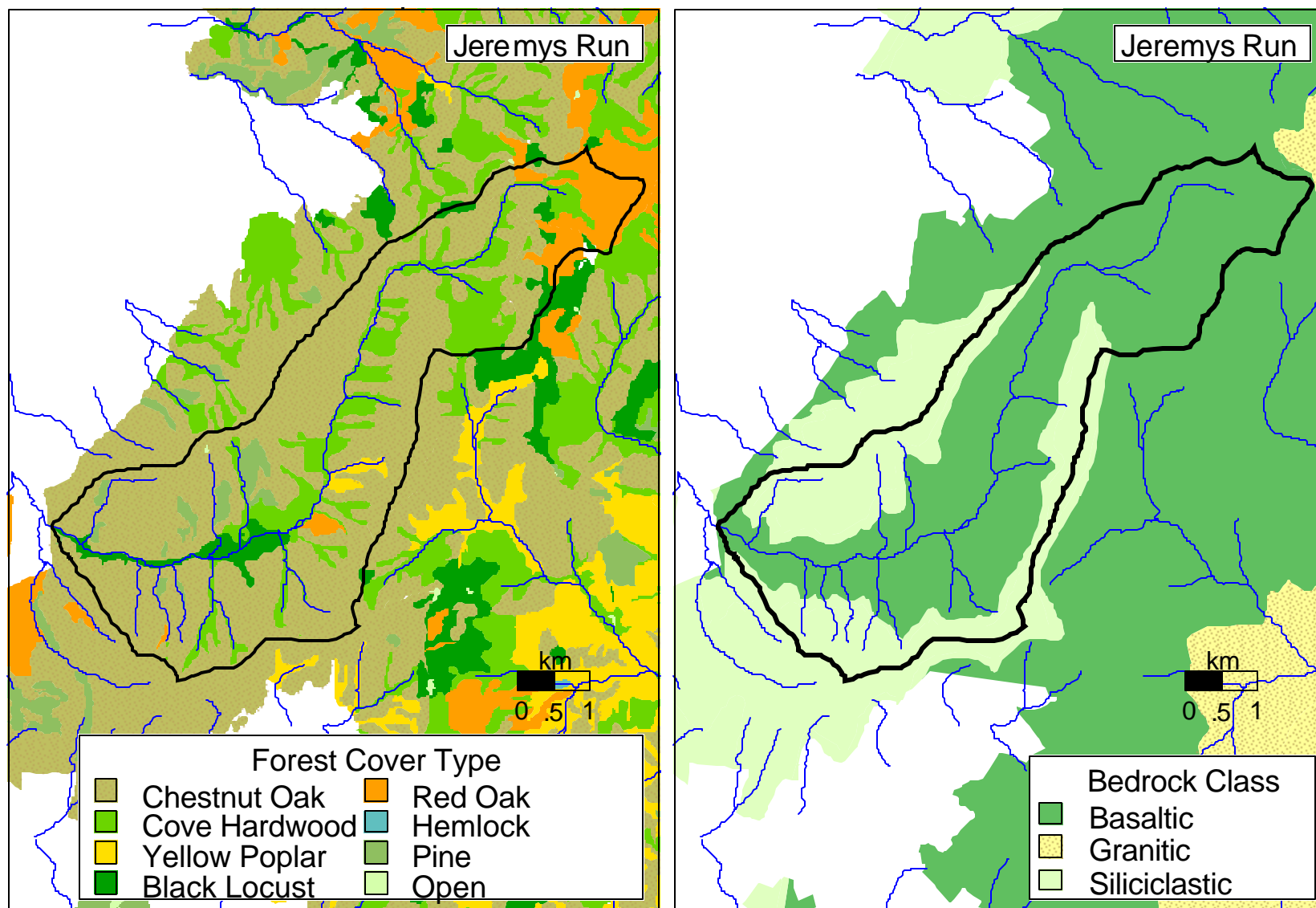


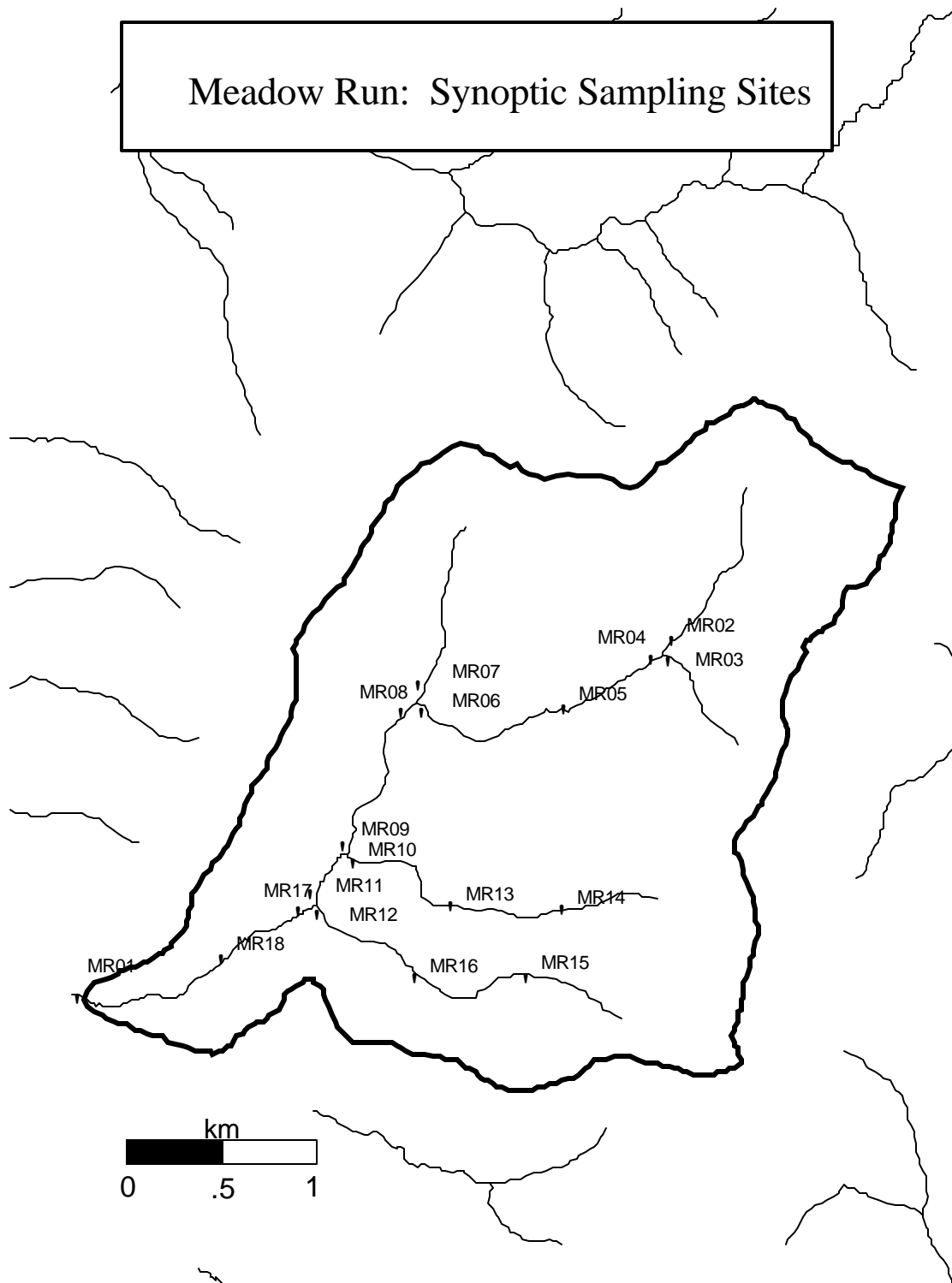
# Appendix - Maps of the SNP:FISH Catchments





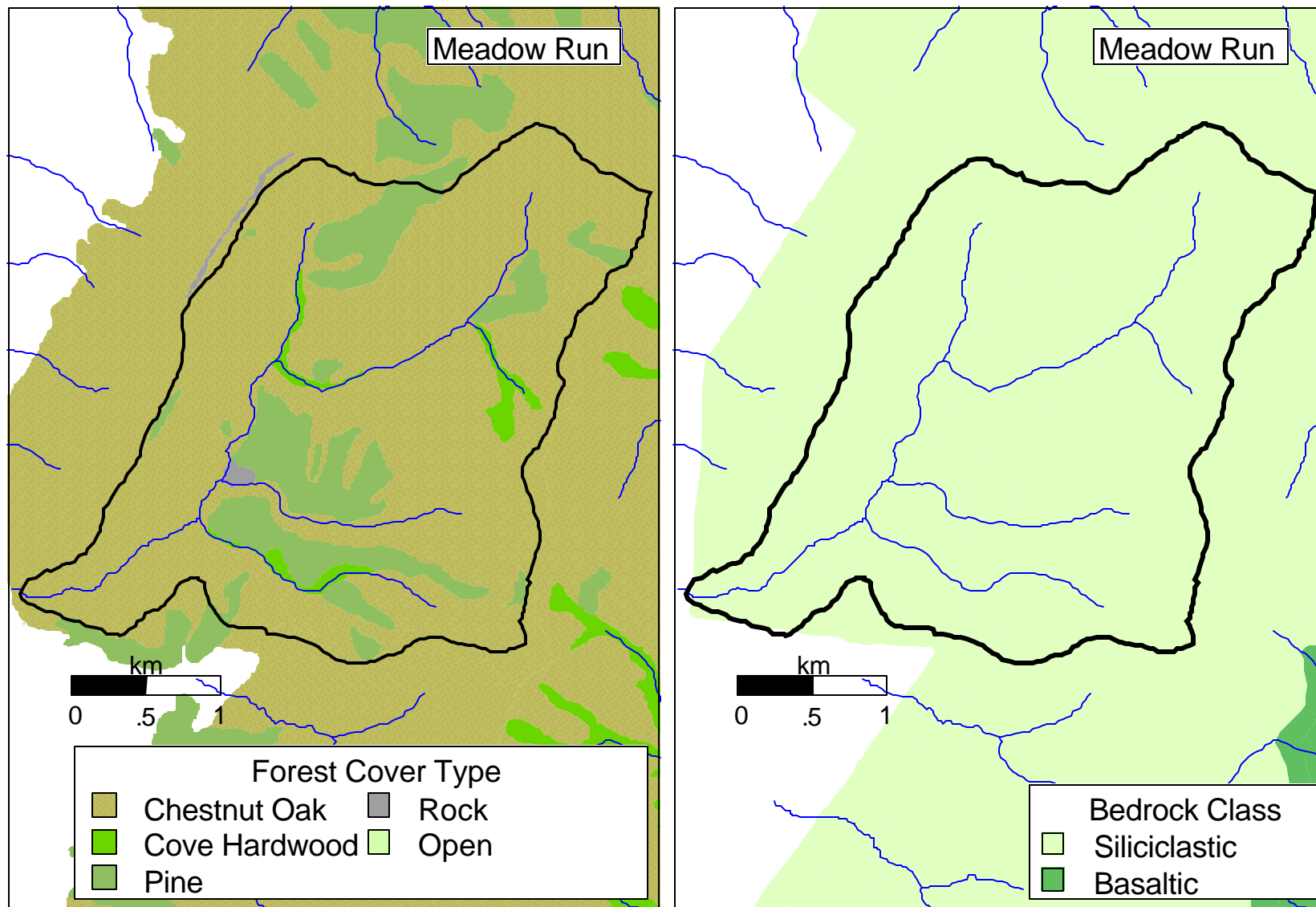
# Appendix - Maps of the SNP:FISH Catchments



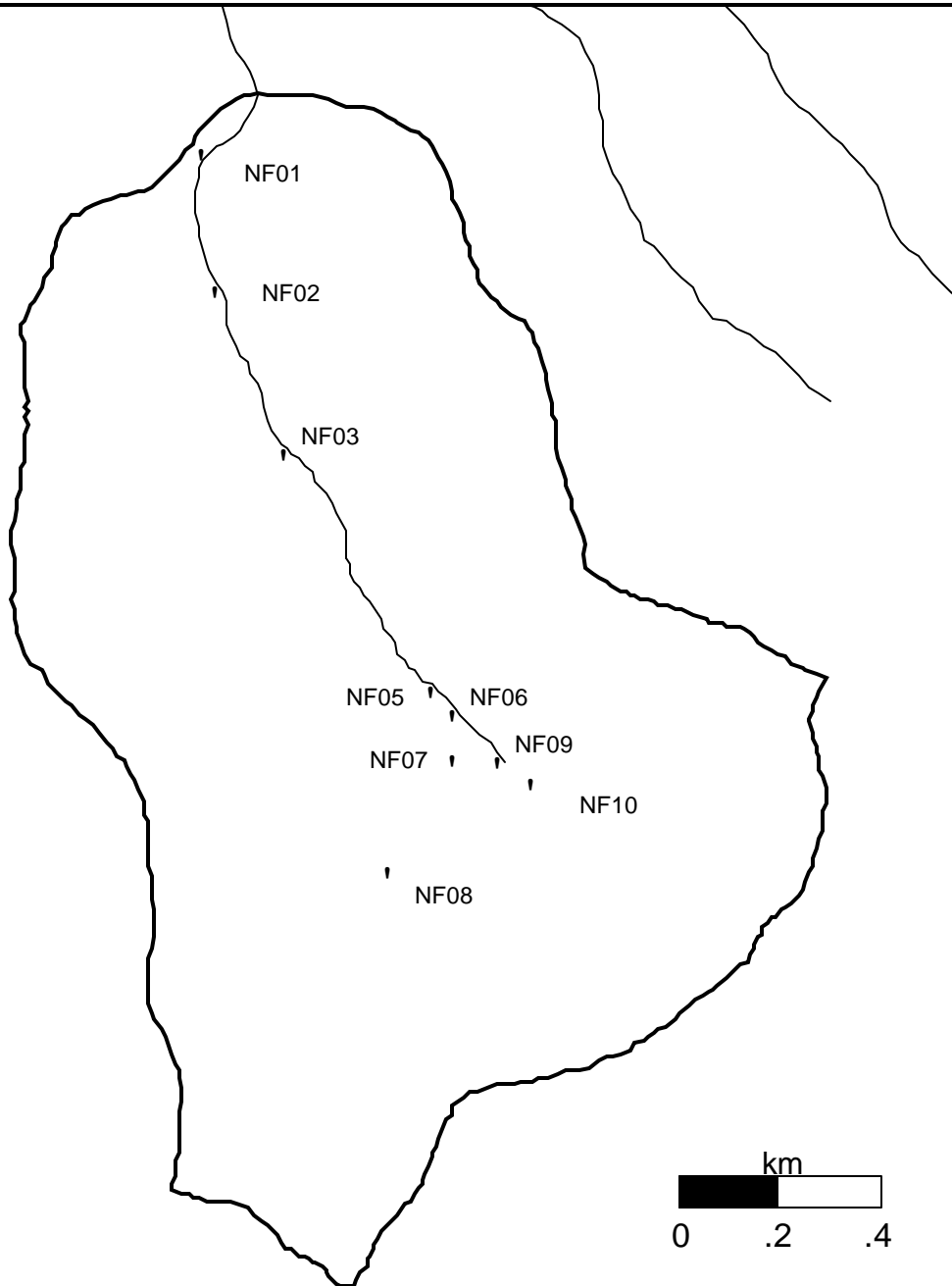




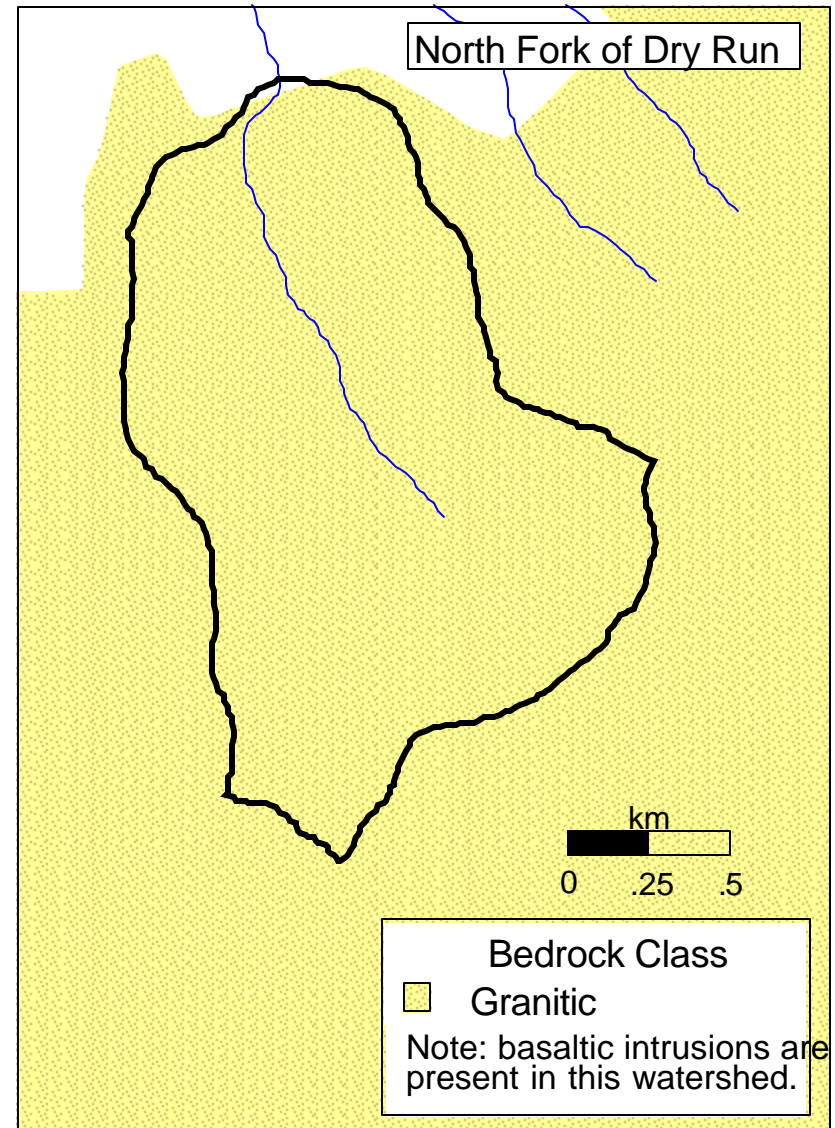
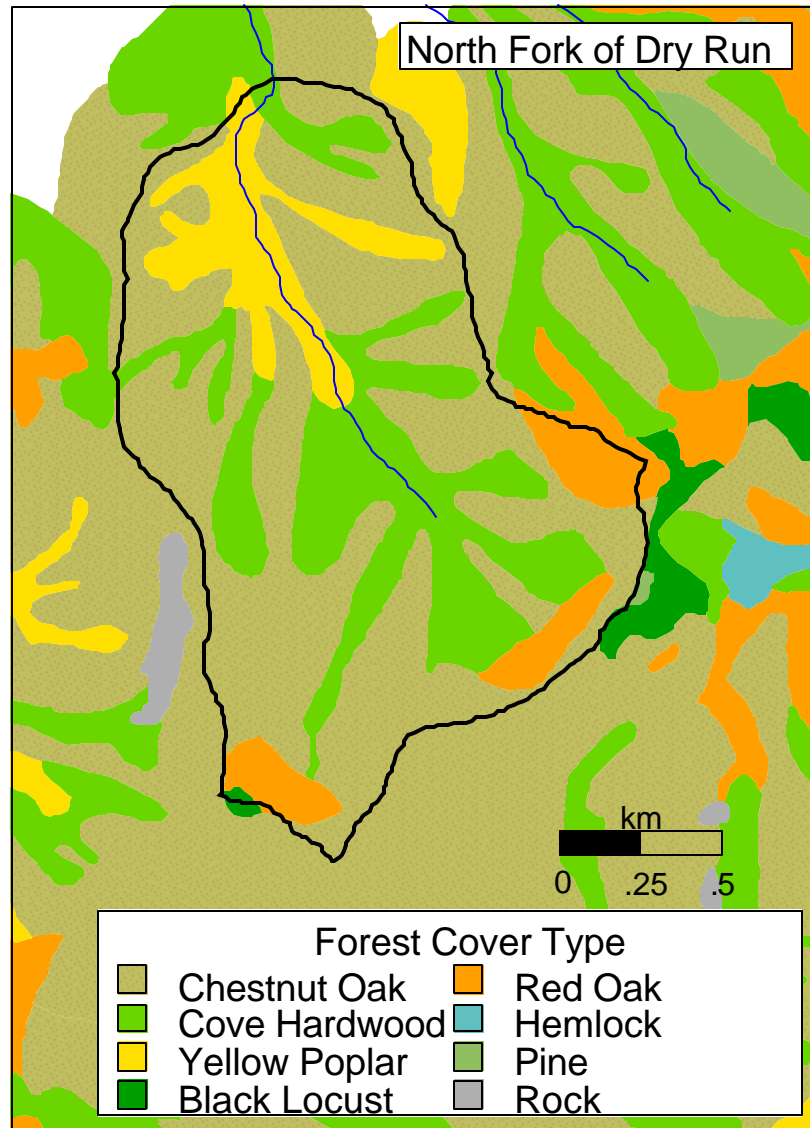
Appendix - Maps of the SNP:FISH Catchments



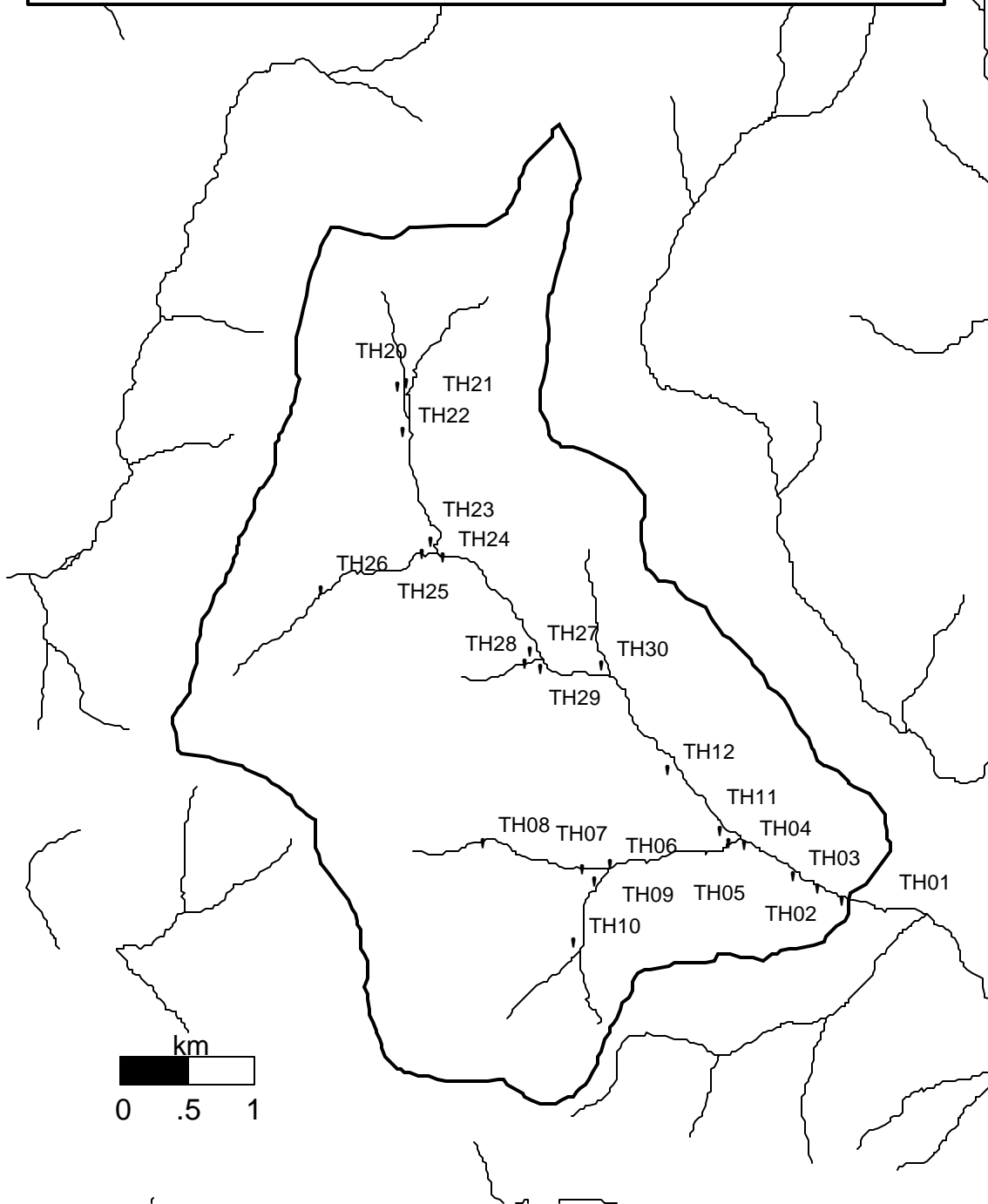
North Fork of Dry Run: Synoptic Sampling Sites

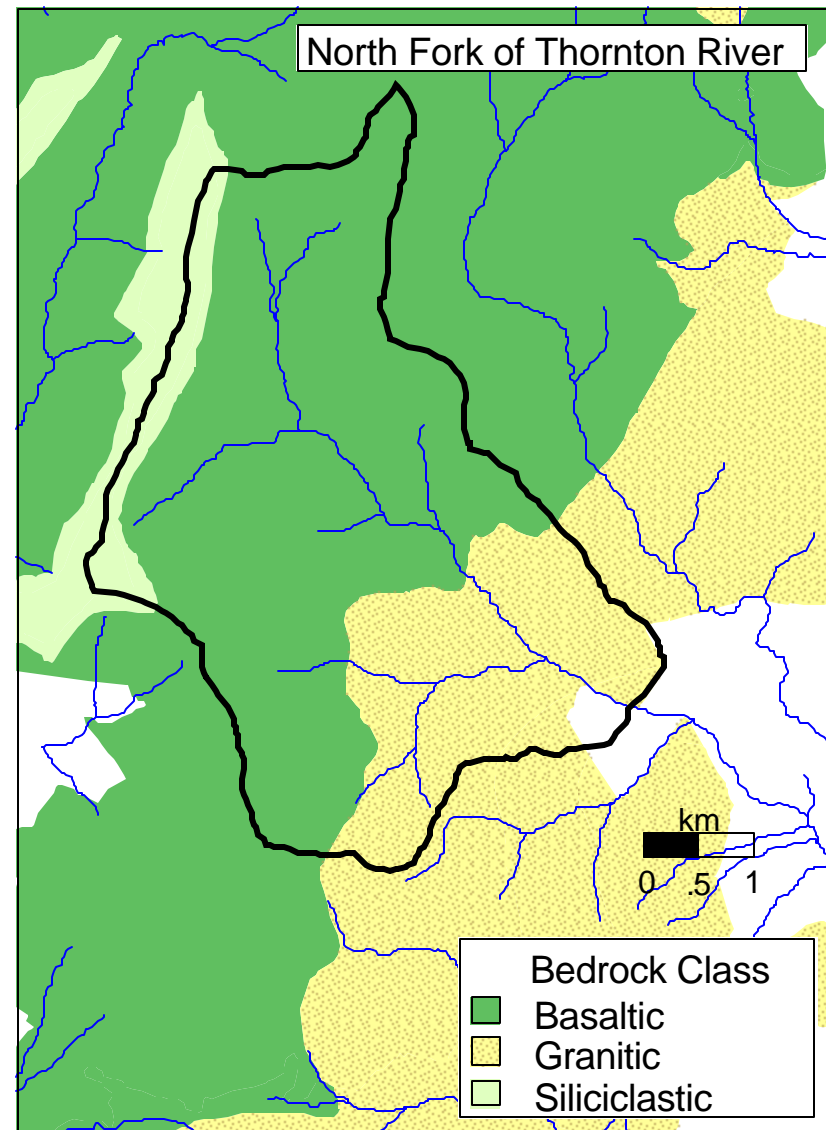
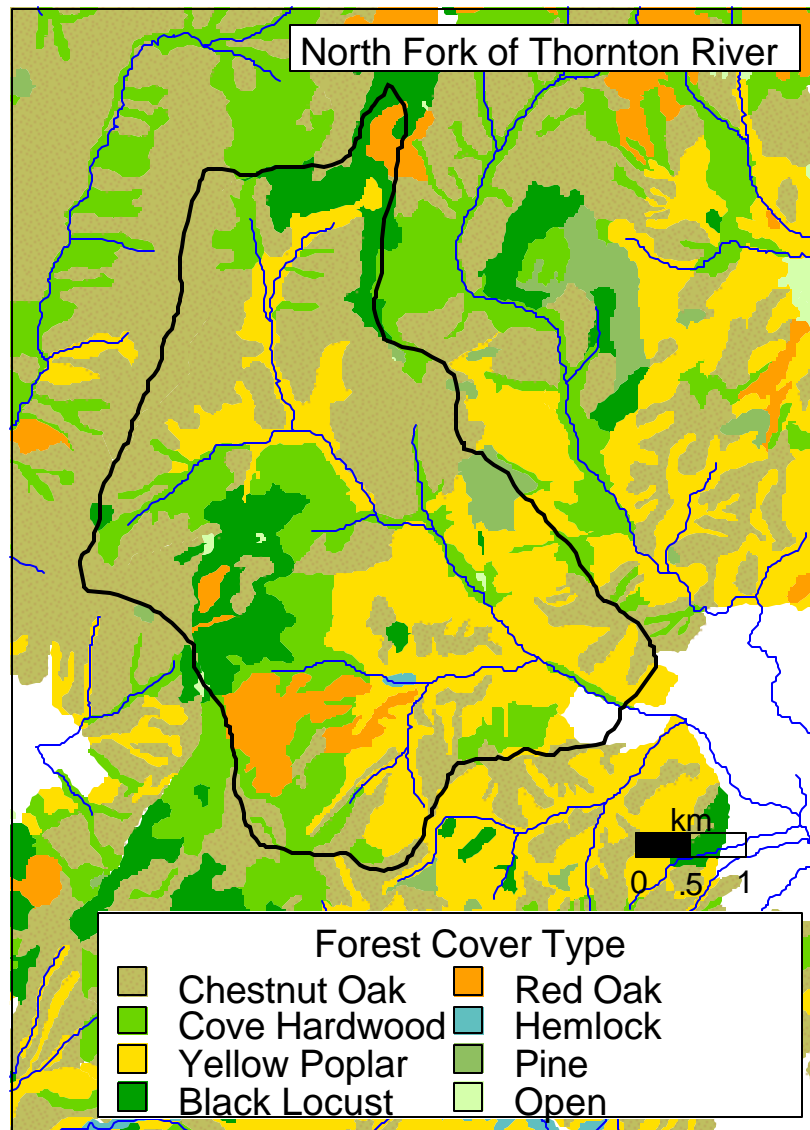


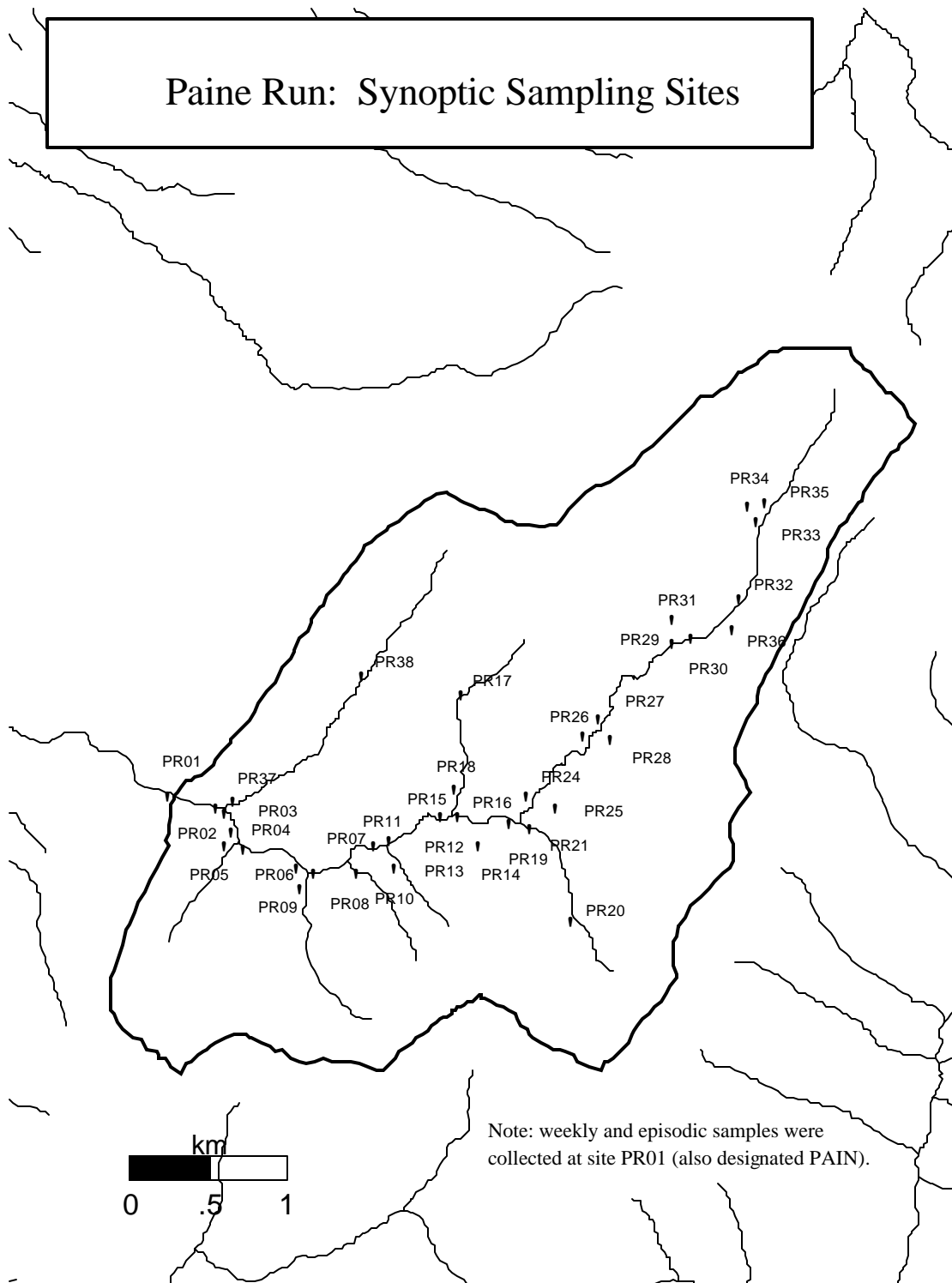
Appendix - Maps of the SNP:FISH Catchments

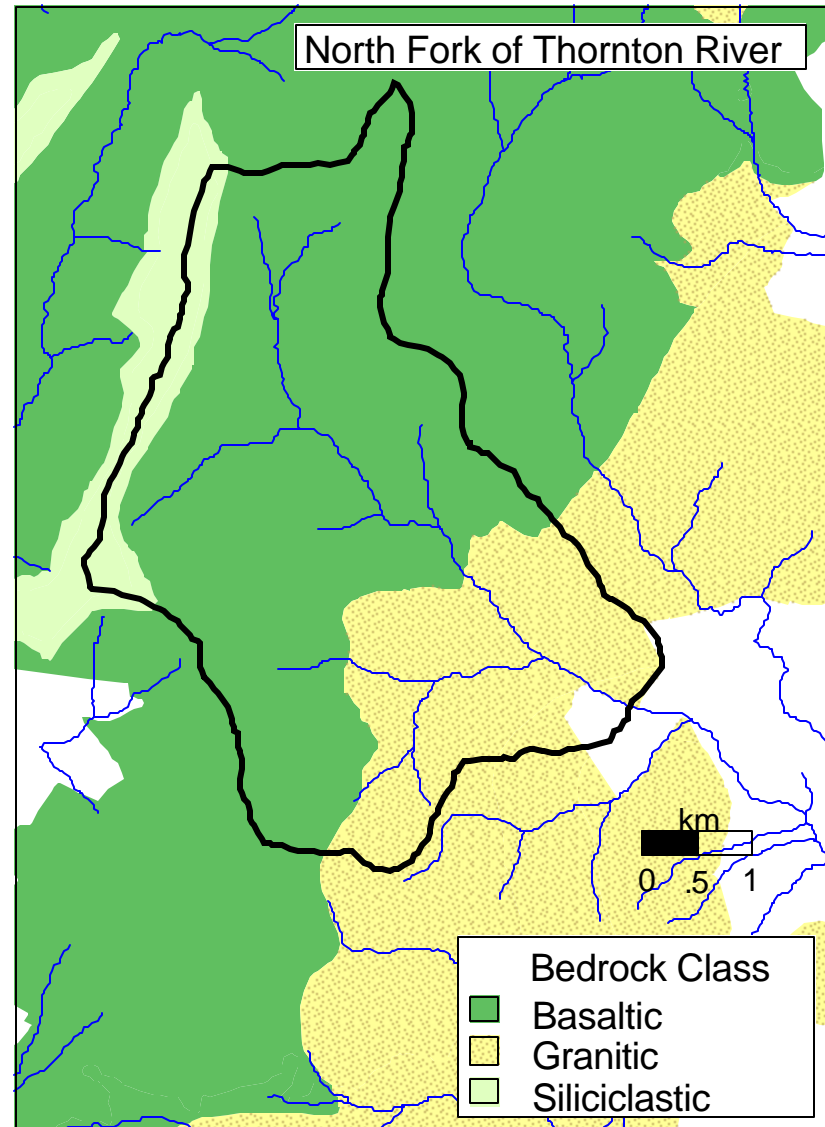
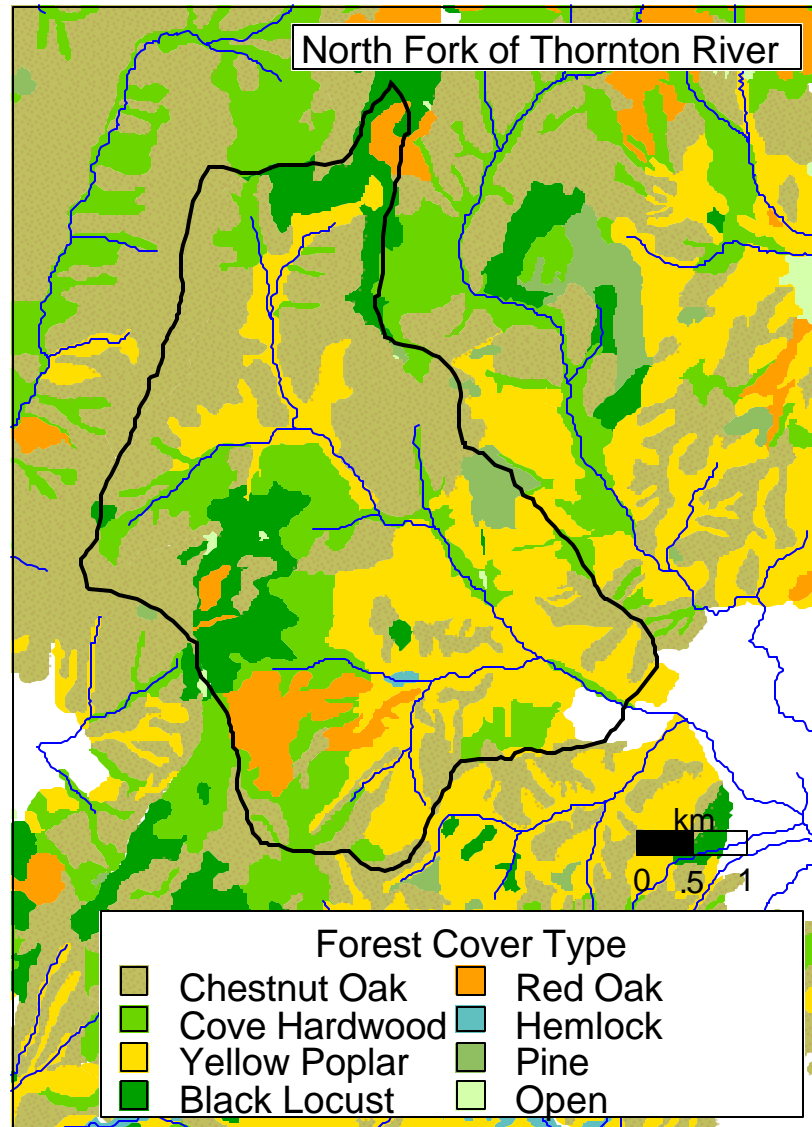


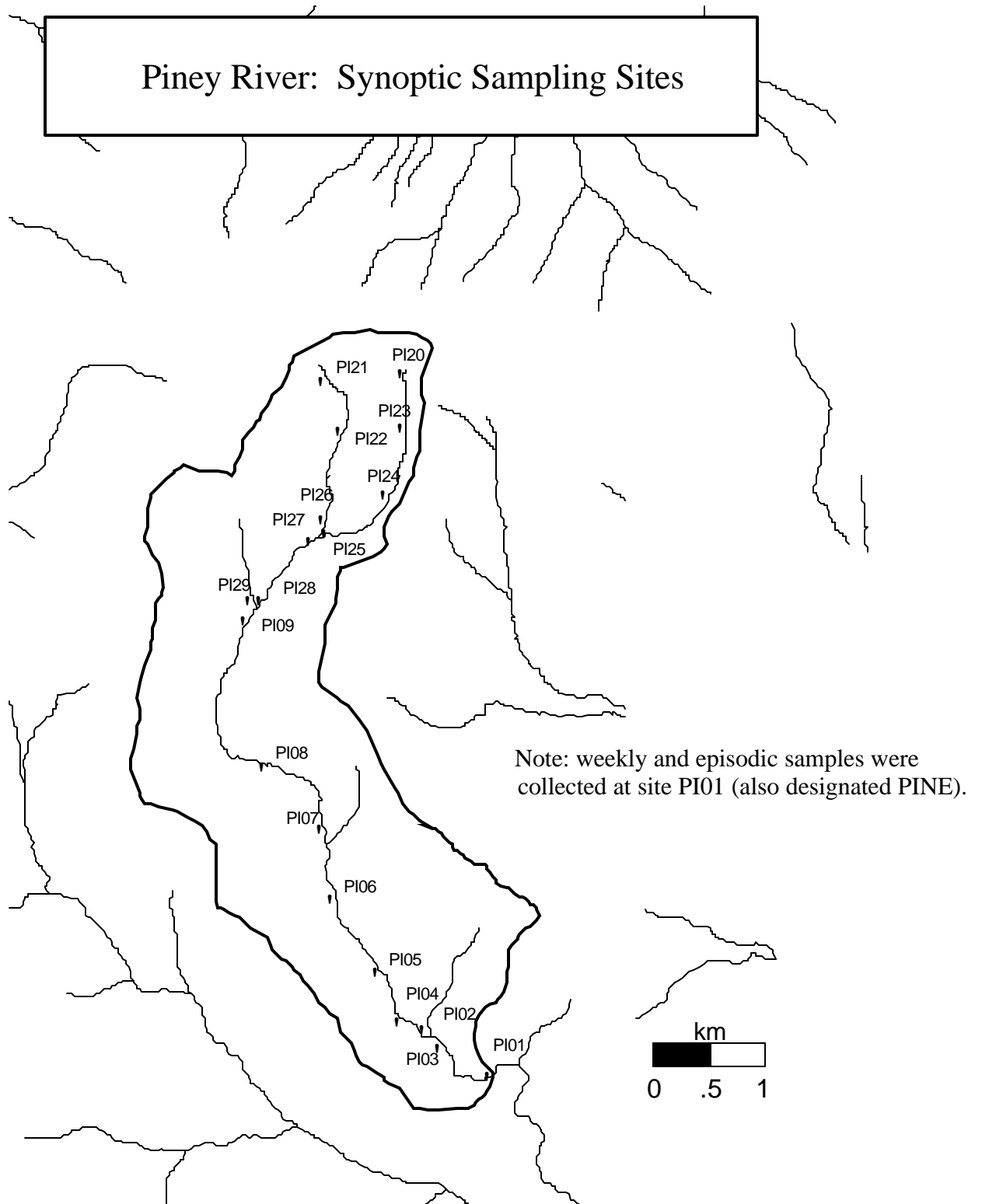
## North Fork of Thornton River: Synoptic Sampling Sites





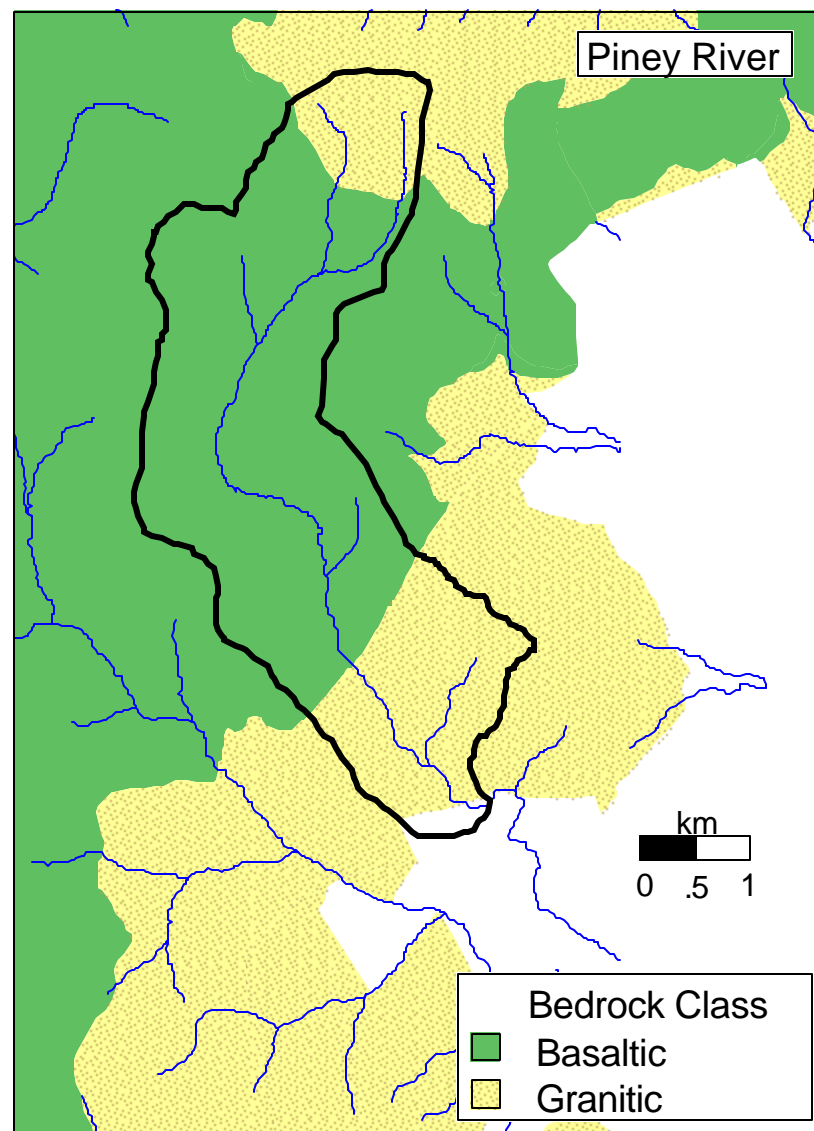
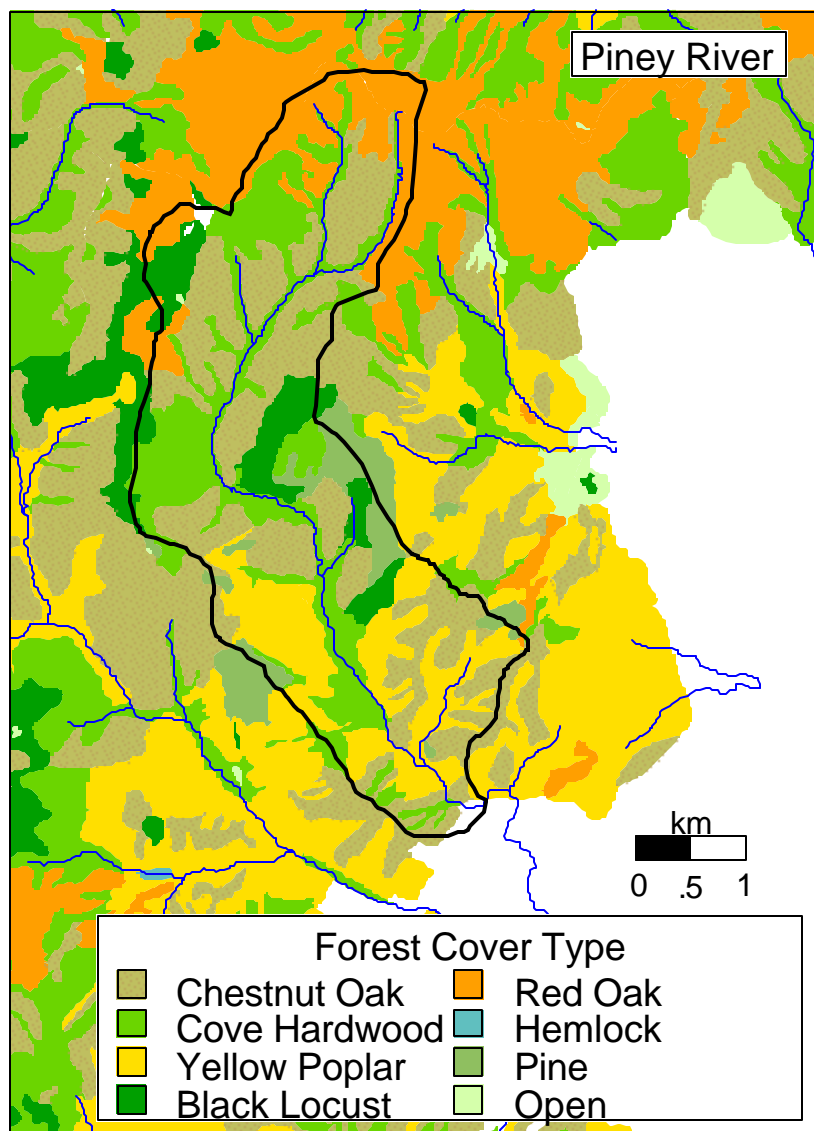






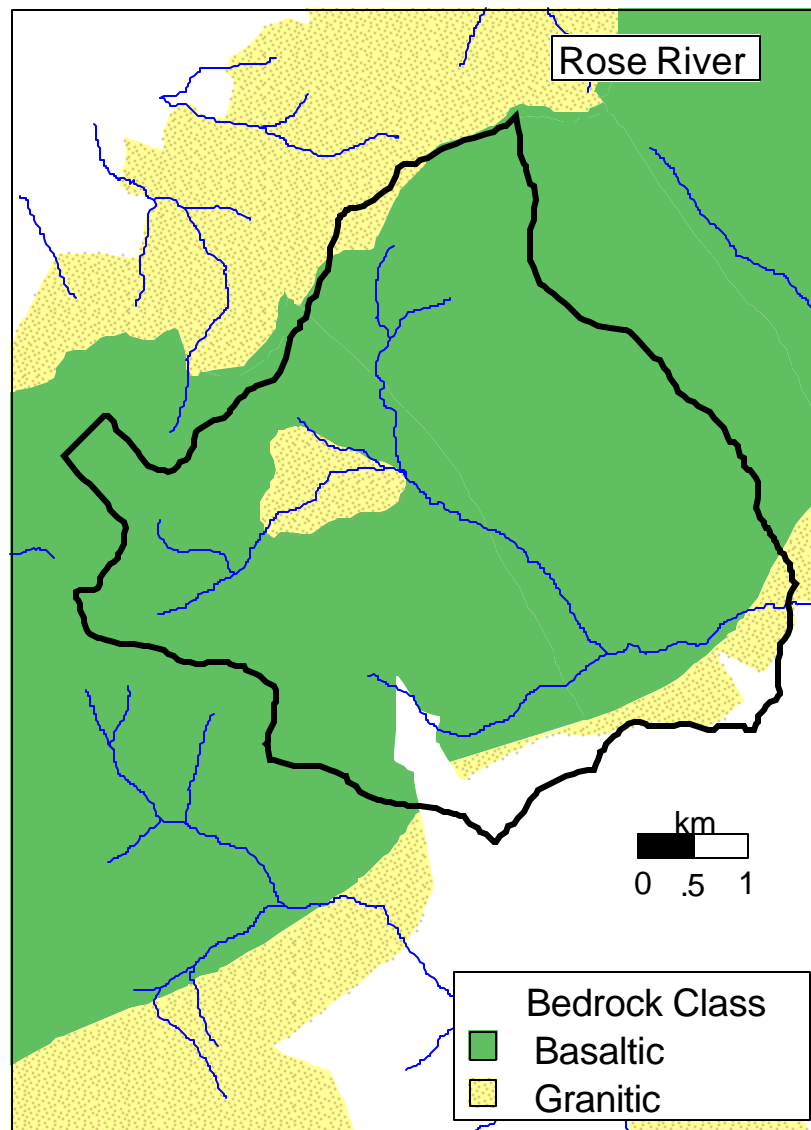
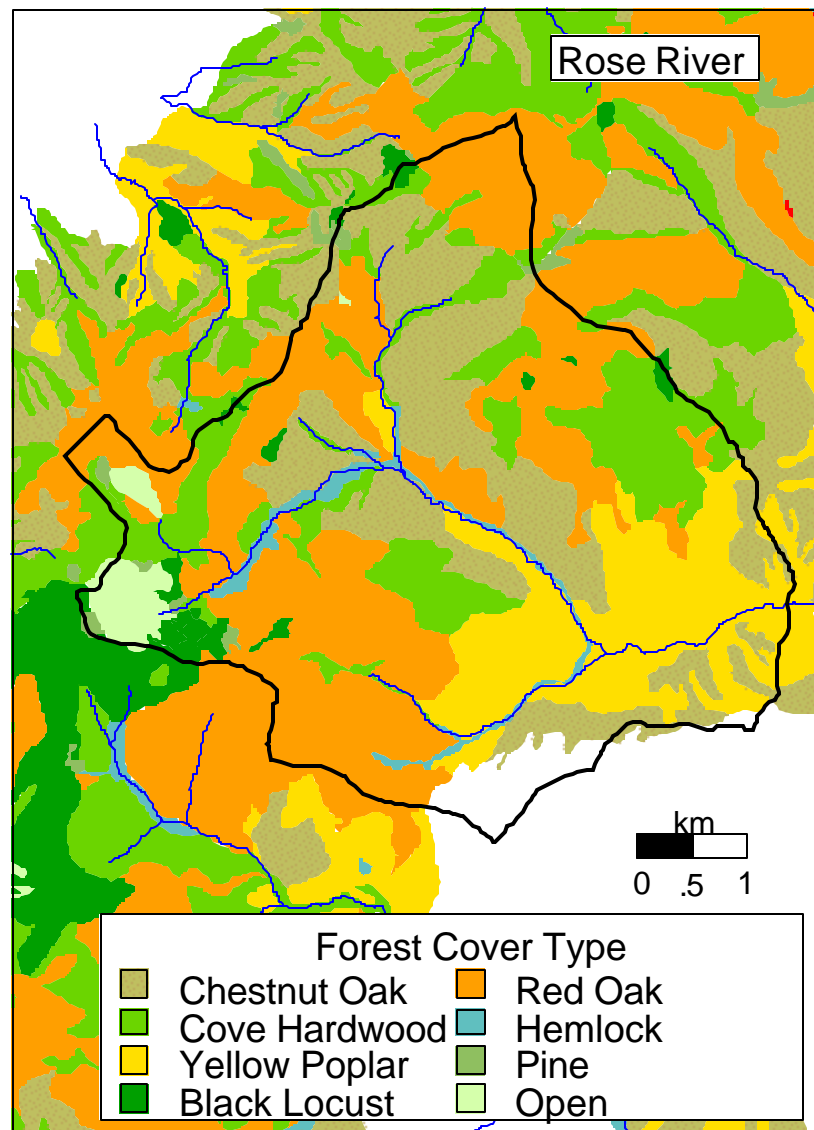


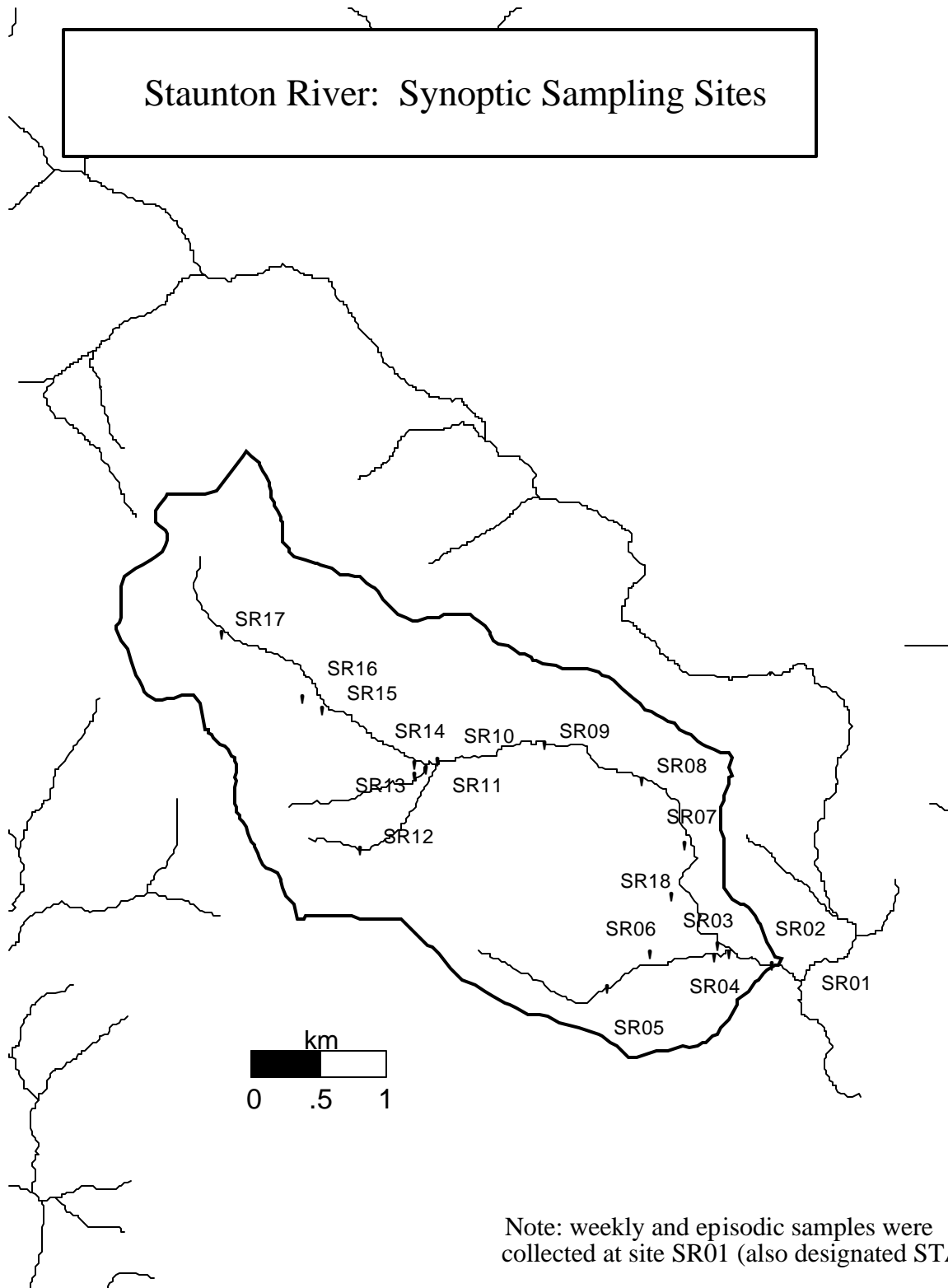
# Appendix - Maps of the SNP:FISH Catchments



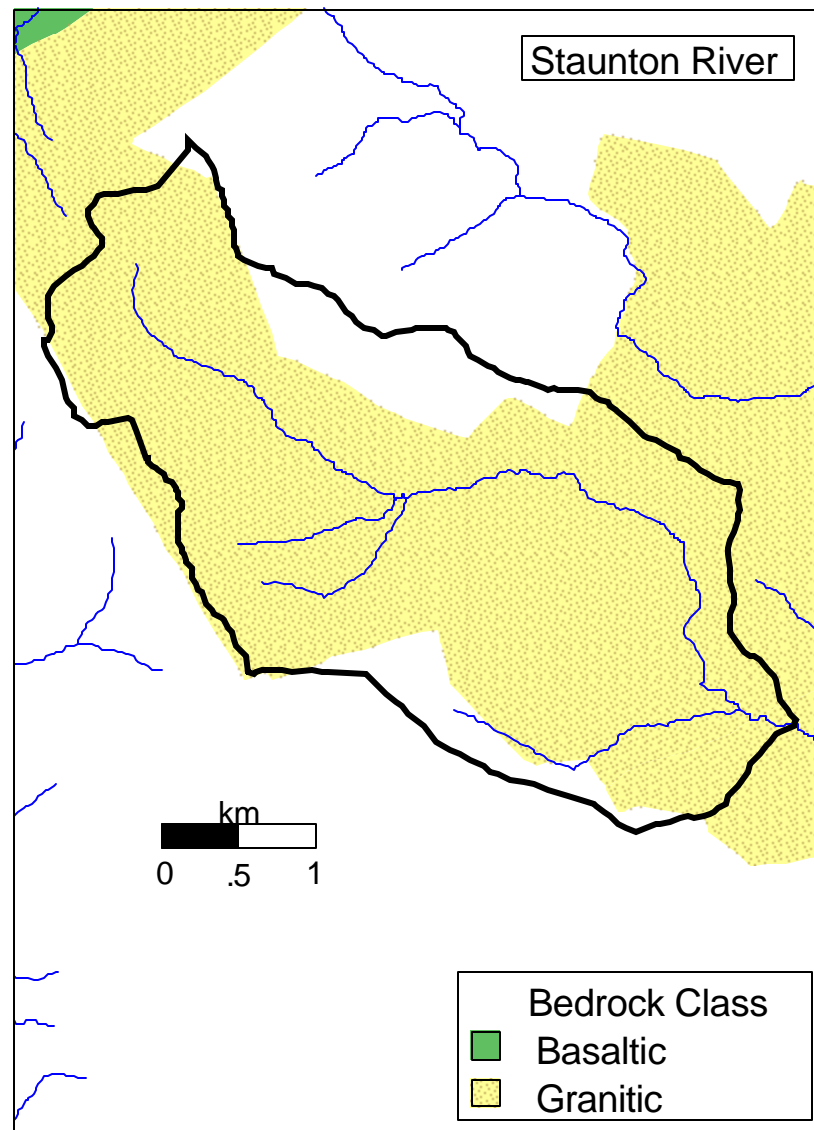
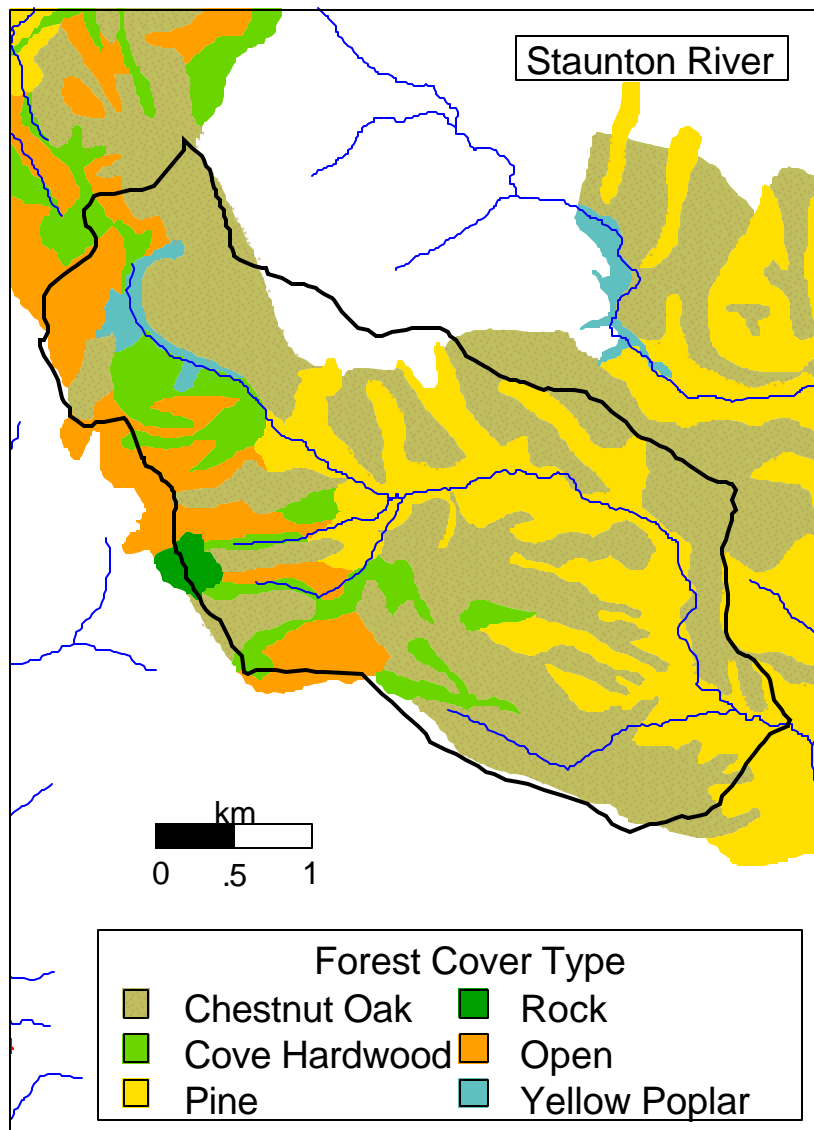


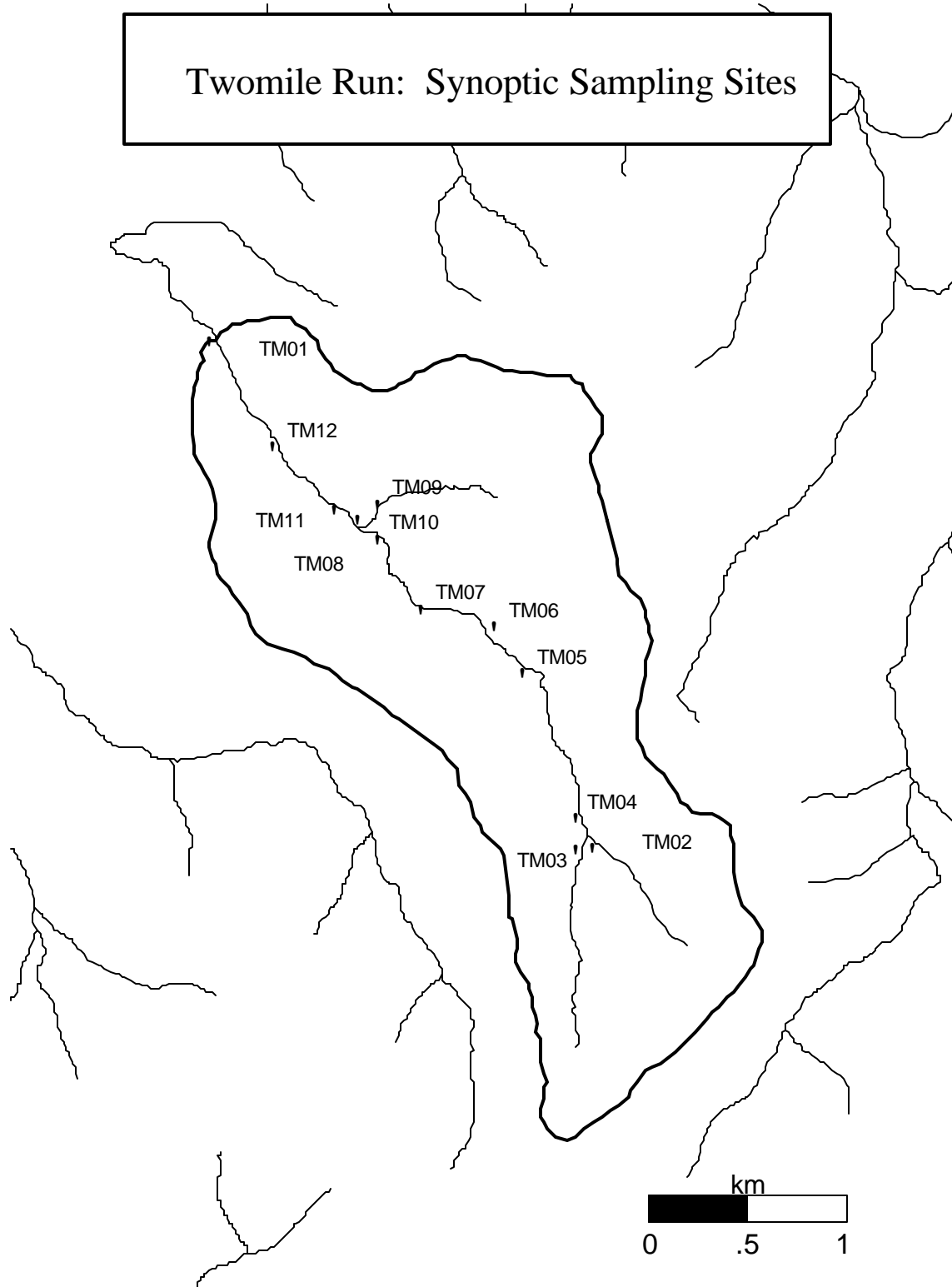
# Appendix - Maps of the SNP:FISH Catchments



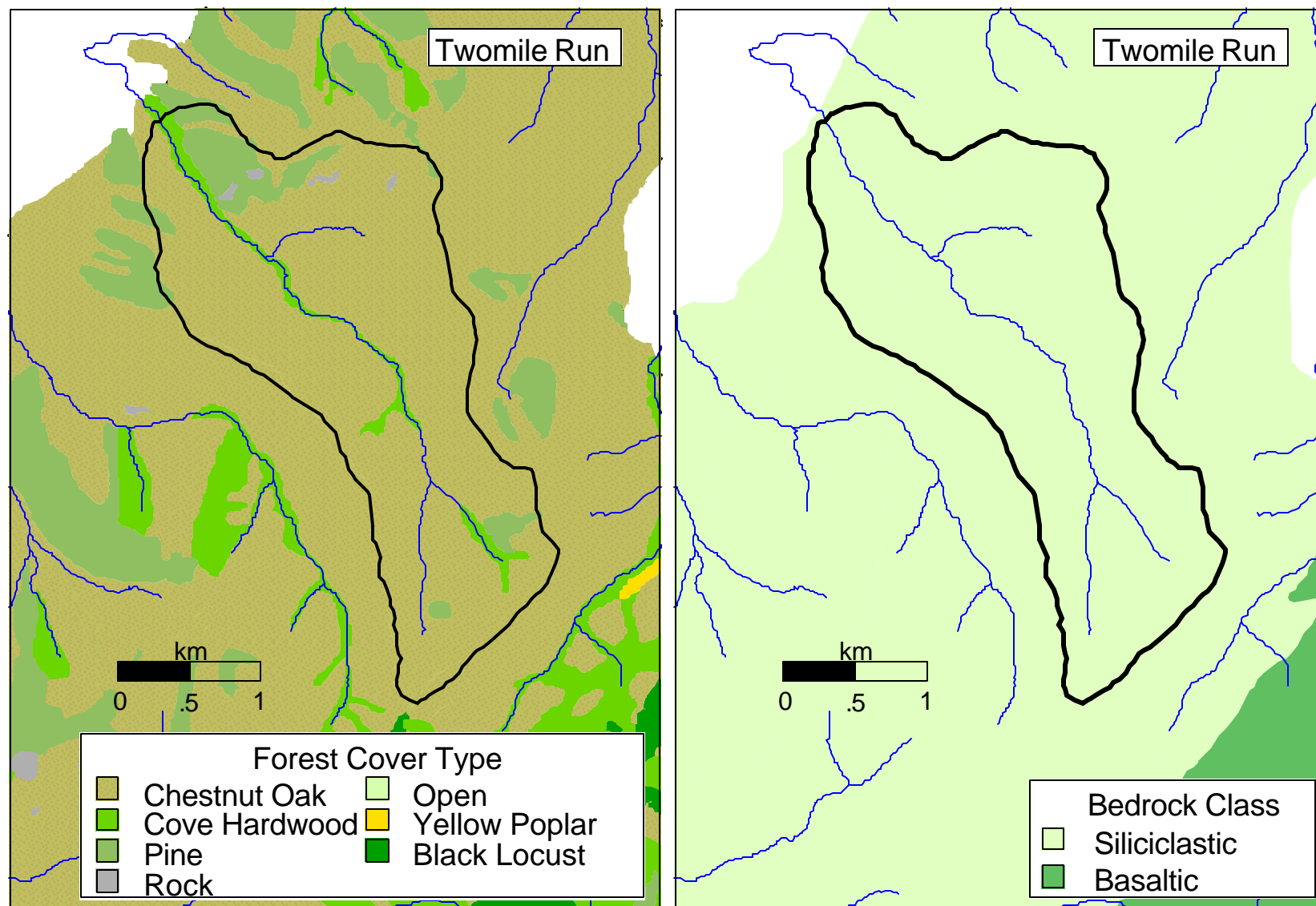


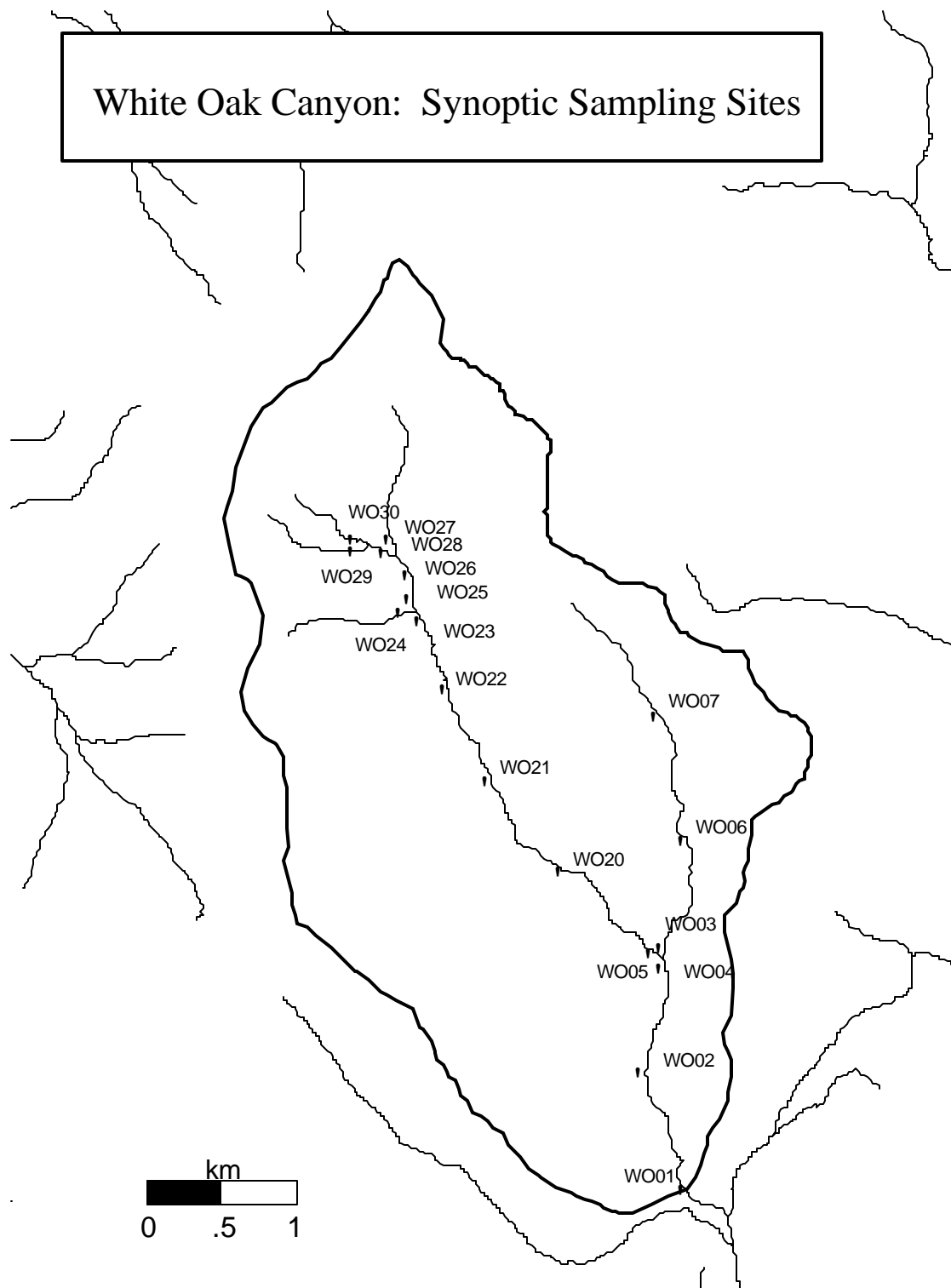
Appendix - Maps of the SNP:FISH Catchments





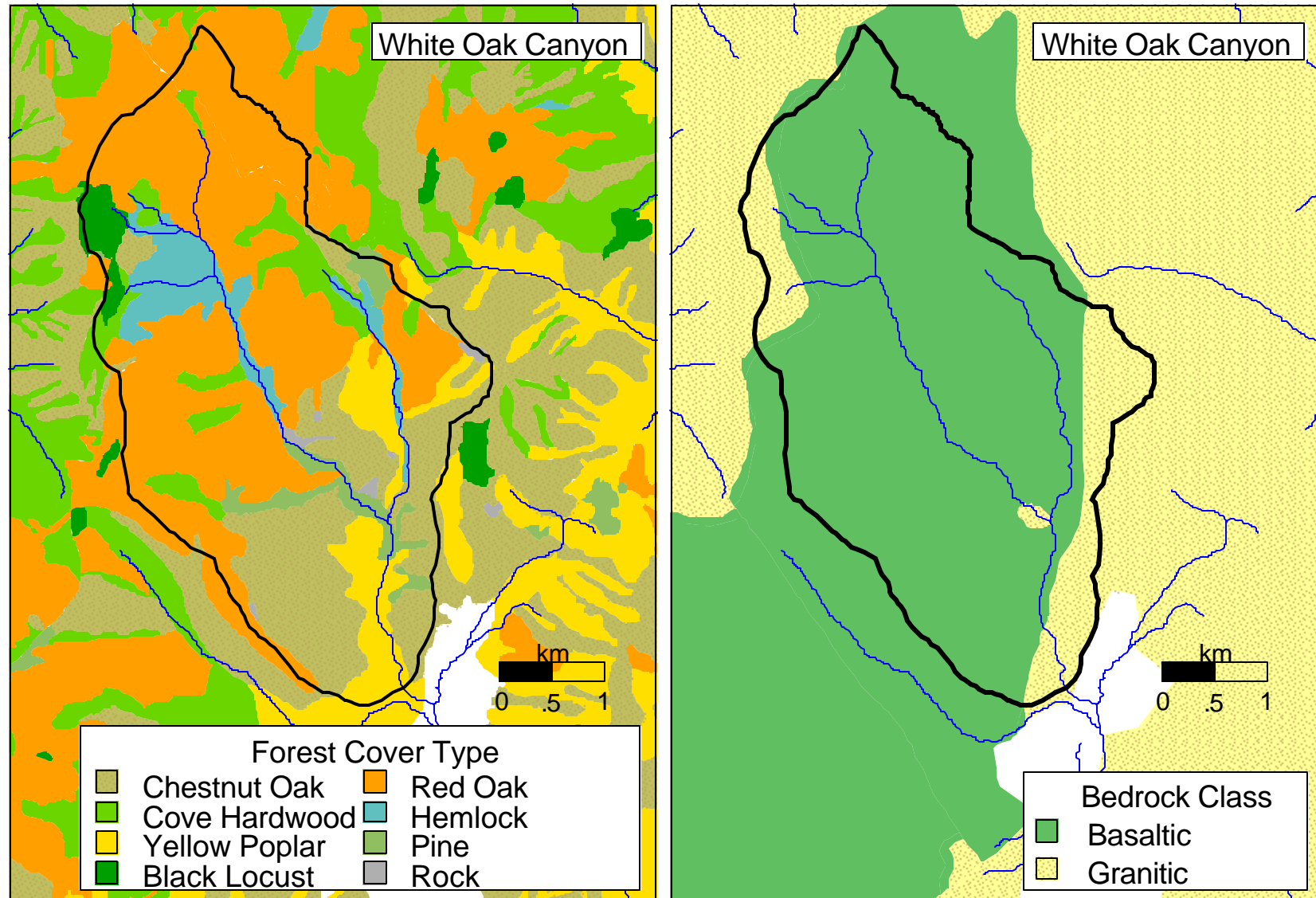
Appendix - Maps of the SNP:FISH Catchments



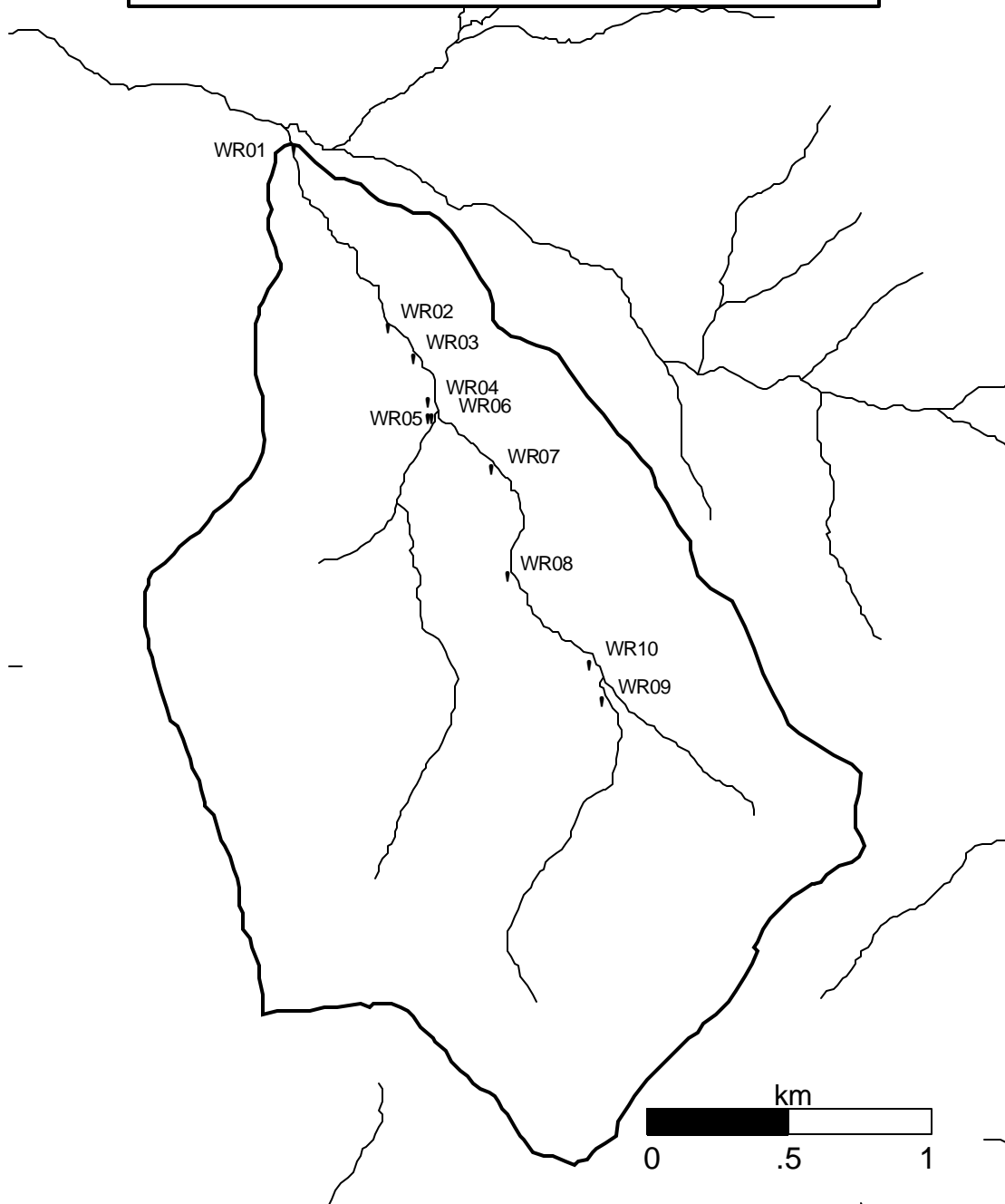




Appendix - Maps of the SNP:FISH Catchments



## White Oak Run: Synoptic Sampling Sites



Appendix - Maps of the SNP:FISH Catchments

